# Effect of proton irradiation and hydriding on strain localisation in zirconium alloys

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**Rhys G Thomas** 

School of Natural Sciences Department of Materials

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# List of abbreviations

DHC	Delayed Hydride Cracking
FEG	Field Emission Gun
SEM	Scanning Electron Microscope
(HR)-DIC	(High Resolution) Digital Image Correlation
EBSD	Electron Backscatter Diffraction
НСР	Hexagonal Close Packed
BCC	Body Centred Cubic
FCC	Face Centred Cubic
BWR	Boiling Water Reactor
PWR	Pressurised Water Reactor
CANDU	Canadian Deuterium Uranium
PCI	Pellet-Cladding Interaction
I-SCC	Iodine Stress Corrosion Cracking
CWSR	Cold Worked Stress Relieved
SPP	Second Phase Particle
CRSS	Critical Resolved Shear Stress
SFE	Stacking Fault Energy
RD	Rolling Direction
TD	Transverse Direction
ND	Normal Direction
YS	Yield Stress
TEM	Transmission Electron Microscopy
UTS	Ultimate Tensile Strength
DPA	Displacements Per Atom
TSSd	Terminal Solid Solubility of Dissolution
TSSp	Terminal Solid Solubility of Precipitation
EDM	Electrical Discharge Machining
OPS	Colloidal Silica Suspension
BSE	Backscattered Electron
CBS	Concentric Backscatter
RDR	Relative Displacement Ratio
BEI	Backscattered Electron Imaging
FFT	Fast Fourier Transform
IPF	Inverse Pole Figure

#### Abstract

Zirconium alloys are utilised by the nuclear industry as a structural and clad material for use in power reactors. The integrity of these components is crucial for efficient and safe generation of power. During operation, neutron irradiation and hydride formation due to corrosion impact yield stress and ductility. The aim of the present PhD project was to characterise the change in deformation behaviour of zirconium alloys exposed to irradiation and hydrides using a combination of high resolution digital image correlation and electron backscatter diffraction techniques.

In order to generate accurate displacement maps using digital image correlation, a pattern at a suitable length scale must be generated on the surface of the sample. The styrene vapour assisted gold remodelling technique was chosen to produce a speckle pattern. The remodelling temperature and time were optimised and strain maps of non-irradiated ZIRLO were created to ensure suitability for investigating sub-grain scale deformation. Proton irradiation was performed as a surrogate for the neutron flux encountered in-reactor and strain localisation was studied in Zircaloy-4 samples irradiated to 0.1 dpa. Dramatically enhanced strain localisation was observed as a result of irradiation and was attributed to the creation of defect-free channels. Due to the texture in zirconium alloys, deformation along different principal directions was performed and slip system activation was quantitatively measured for both non-irradiated and irradiated conditions. Differing slip system activation was observed for loading along the rolling direction compared loading along the transverse direction, however no significant change in slip system activation was observed due to irradiation. Finally, strain localisation in a sample containing hydrides induced by cathodic charging and homogenisation heat treatment was investigated. The average amount of strain observed within hydrides and second phase particles was lower than that in the matrix and shear bands were observed to terminate at transgranular hydrides.

As well as providing an improved understanding of the impact of irradiation and hydrides on strain localisation in zirconium alloys, the methods developed will allow further investigation of deformation behaviour in corrosion-susceptible materials. Quantitative displacement maps and slip system activation data will allow for validation of crystal plasticity models, used to predict deformation behaviour of components subject to inreactor degradation.

## Declaration

I declare that no portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

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## **Publications and presentations**

This thesis is presented in journal format, comprising of a manuscript draft and the following two papers published in peer reviewed journals:

D. Lunt, A. Orozco-Caballero, <u>R. Thomas</u>, P. Honniball, P. Frankel, M. Preuss, J.Q. da Fonseca. *Enabling high resolution strain mapping in zirconium alloys*. Material Characterization, Volume 139, May 2018, Pages 355-363.

<u>R. Thomas</u>, D. Lunt, M.D. Atkinson, J.Q. da Fonseca, M. Preuss, F. Barton, J O'Hanlon, P. Frankel. *Characterisation of irradiation enhanced strain localisation in a zirconium alloy*. Materialia, Volume 5, March 2019, 100248

The thesis also contains a manuscript accepted for publication in internationally recognised peer reviewed conference proceedings:

<u>R. Thomas</u>, D. Lunt, M.D. Atkinson, J. Quinta da Fonseca, M. Preuss, F. Barton, J O'Hanlon, P. Frankel. *Effect of loading direction on slip and twinning in an irradiated zirconium alloy*. ASTM Zirconium in the Nuclear Industry: Nineteenth International Symposium.

The author of this thesis also contributed towards the following manuscripts:

X. Xu, D. Lunt, <u>R. Thomas</u>, R. Prasath Babu, A. Harte, M. Atkinson, J.Q. da Fonseca, M. Preuss. *Identification of active slip mode in a hexagonal material by correlative scanning electron microscopy*. Acta Materialia, Volume 175, 15 August 2019, Pages 376-393.

The work in this thesis has also been presented at a number of international conferences:

May 2019	Oral presentation at ASTM Zirconium in the Nuclear Industry: Nineteenth				
	International Symposium, Manchester, UK.				
Dec 2018	Poster presentation at the Rolls-Royce Nuclear UTC Christmas Seminar				
Oct 2018	Poster presentation at NuMat, Seattle, WA				
	3 <sup>rd</sup> place NuMart photo competition				
	Photo featured on cover of Journal of Nuclear Materials 2019				
Sep 2018	Oral presentation at the International Workshop on Mechanistic Behaviour				
	of HCP alloys, Oxford, UK				
Apr 2018	Oral presentation at HEXMAT workshop, London, UK				
Nov 2017	Poster presentation at the Rolls-Royce Nuclear UTC Annual Review, Derby,				
	UK				
	'Best Poster' award				
Jun 2017	Session chair at the National Student Conference in Metallic Materials,				
	Sheffield, UK				
Mar 2017	Poster presentation at the MPC 15 <sup>th</sup> Anniversary Conference, Manchester,				
	UK				
	'Best Poster' award				
Feb 2017	Oral presentation at TMS, San Diego, CA				
Oct 2016	Poster presentation at the Rolls-Royce Nuclear UTC Annual Review, Derby,				
	UK				
Jul 2016	Oral presentation at Junior Euromat, Lausanne, Switzerland				
	'Best Oral Presentation in Structural Materials' award				
Jun 2016	Oral presentation at the National Student Conference in Metallic				
	Materials, Sheffield, UK				
Apr 2016	Poster presentation at the International Workshop on Mechanistic				
	Behaviour of HCP alloys, Oxford, UK				
Oct 2015	Poster presentation at the Rolls-Royce Nuclear UTC Annual Review, Derby,				
	UK				
Jun 2015	Poster presentation at the National Student Conference in Metallic				
	Materials, Sheffield, UK				

#### 1. Introduction

Zirconium alloys are primarily used by the nuclear industry as fuel cladding in light water reactors and pressure tubes in heavy water reactors. The fuel in such reactors normally takes the form of small cylindrical pellets that are stacked and encased by a thin-walled tube known as the cladding, as shown in Figure 1.1a [1]. These single rods are bundled to form assemblies (Figure 1.1b), which provide a rigid structure for transportation and handling. Assemblies are arranged in a reactor core (Figure 1.1c) in such a way as to optimise parameters such as fuel utilisation, temperature and reactivity [2]. The structural integrity of these components is crucial to the safe, efficient operation of the reactor. As well as holding the fuel pellets in place, the cladding should effectively conduct heat from the fuel to the coolant, prevent the escape of any fission products and be as neutron transparent as possible. Additionally, the material should be able to withstand a hot (280-330°C) aqueous environment and neutron bombardment for many years whilst retaining adequate strength [1–4].



Figure 1.1. Schematic drawing of a) fuel rod, b) fuel assembly and c) pressurised water reactor [2,5].

Many alloys could perform well at any one of the tasks, but zirconium alloys have a combination of properties that make it well suited for use as a structural material inside a nuclear reactor [6]. The low thermal neutron absorption cross-section of 0.18 barn was the initial driving force for the development of zirconium alloys as a structural material for the American nuclear reactor fleet [2]. This is because a material with a low thermal neutron

absorption cross-section means more neutrons are available to cause fission and less <sup>235</sup>U is required. This is also important for non-proliferation and cost reduction purposes in civil nuclear power stations. Beside this, zirconium alloys have reasonable strength at reactor operating temperature (around 300°C) and the melting temperature of 1845°C is many times that encountered under normal operating conditions [7]. Alloy development over the past decades, specifically the optimisation of alloying content, has significantly improved resistance to corrosion by high-temperature water.

Although zirconium is abundant in the Earth's crust, it is relatively expensive to produce. This is because the ores in which it is found contain hafnium, which must be removed as its neutron absorption cross-section is 1000x that of zirconium [2]. Due to its high affinity to oxygen, nitrogen and hydrogen, which are detrimental to material properties, they must also be strictly controlled during processing, which increases cost. This is also an issue during operation, where hydrogen can be absorbed by the cladding as a result of corrosion, which then precipitates as hydrides due to the low solubility of hydrogen in zirconium [6]. With no external stress present, hydrides precipitates in the circumferential direction due to the texture of the material [8]. Under an applied stress, which could arise as a result of thermal expansion of the fuel pellets or fission gas build-up for example, the hydrides can reorient. In a radial configuration, they can deteriorate the mechanical integrity of the cladding [8].

Even if the average concentration of hydrogen is not above the solubility limit, the stress concentration provided by a defect or notch can lead to an increased local hydrogen concentration and hydride precipitation [9]. This is due to the tendency of hydrogen to diffuse towards cold regions and hydrostatic tensile stresses. Subcritical crack initiation can then occur and the stress field associated with this crack will result in a further increase in hydrogen concentration, hydride precipitation and advancement of the crack, known as delayed hydride cracking (DHC) [10]. During service, neutron irradiation causes defect structures to form, which increase the strength and decrease the ductility of the material, as a function of fluence [11,12]. This can also have a deleterious effect on delayed hydride cracking velocity [13].

Examining the assemblies in service is not feasible and replacement due to failure is expensive. Therefore, to maintain safe and economic operation, the design life of the components must be accurately determined. Understanding the degradation mechanisms of the material and their dependence on operating condition and initial material properties is crucial. The advent of new techniques that allow strain localisations incurred during deformation to be measured on the sub-grain scale are key to further developing this understanding, but as of yet, no measurements have been made on irradiated zirconium alloys.

#### 1.1. Aims

The work presented in this thesis concerns the use of scanning electron microscopy (SEM)based techniques to assess the impact of irradiation and hydrides on the deformation behaviour of commercial zirconium alloys. Local strain measurements from digital image correlation (DIC) and grain orientation from electron backscatter diffraction (EBSD) will be combined using Python scripting. This will allow the effect of underlying microstructure on strain localisation to be accurately measured on a sub-grain scale for hundreds of grains.

- Recent work on patterning of corrosion susceptible samples will be built on to reliably generate a high contrast pattern on zirconium alloys, with features of a suitable size to gain low-noise measurements of sub-grain scale strain.
- In-reactor degradation due to neutron irradiation will be emulated with proton irradiation. The effect of irradiation and loading direction on strain heterogeneity and slip system activation will be assessed.
- By electrochemical hydrogen charging, the impact of embedded hydrides and second phase particles on strain patterning and slip system activation will be quantitatively measured. In particular, the matrix-hydride boundaries will be examined.

### **1.2.** Thesis structure

The structure of each part of the thesis is summarised below:

• The next section will consist of a **literature review** to provide context for the manuscripts. Details that are better established will first be briefly discussed. More

recent literature concerning the deformation of zirconium alloys and particularly the effect of irradiation and hydrides will then be evaluated.

- All the **experimental methods** used in the manuscripts will be detailed in the subsequent section.
- The first manuscript presents the optimisation of the styrene-remodelling technique for generating a pattern with high contrast, suitable for DIC, on the surface of zirconium alloys. As well as discussing the change in pattern as a function of time, preliminary strain maps of ZIRLO are also presented.
- Following further optimisation of imaging parameters, the second manuscript presents the first strain maps of irradiated Zircaloy-4 in a letters-style publication. The deformation behaviour is related to the microstructure using EBSD.
- The **third manuscript** presents a more detailed, quantitative analysis of the impact of both irradiation and loading direction on the deformation behaviour and slip system activity of Zircaloy-4.
- By introducing hydrogen into the material, the impact of delta hydrides and second phase particles on strain localisation are discussed in the **fourth manuscript**.
- Finally, the conclusions will be summarised and future work identified.

#### 2. Literature Review

This section starts by discussing zirconium metallurgy, focussing on common zirconium alloys compositions and second phase particles in the context of fuel cladding degradation mechanisms. Next, plastic deformation mechanisms and the effect of hexagonal crystal anisotropy on bulk texture during processing is discussed. The effect of neutron irradiation on material properties and the use of proton irradiation as a surrogate is evaluated. Previous studies on the effect of hydrogen ingress and hydrides on the mechanical properties of zirconium are reviewed. Literature concerning hydrogen charging, using both cathodic and gaseous methods, is reviewed and the importance of cooling rate is discussed. Finally, the digital image correlation technique is described, different patterning technique are compared and existing low-resolution digital image correlation studies on zirconium are critically evaluated.

#### 2.1. Zirconium metallurgy

Commercially pure zirconium metal at room temperature and atmospheric pressure exhibits a hexagonal close-packed (HCP) crystallographic structure, known as the  $\alpha$ -phase, with lattice parameters a = 3.233 Å and c = 5.149 Å [14,15]. Therefore, a c/a ratio of 1.593 is observed, which is lower than the ideal sphere packing value of 1.633 [16]. At 865°C, an allotropic phase transformation to the body-centred cubic (BCC)  $\beta$ -phase occurs, before the metal melts at 1865°C [6]. At pressures over around 1 GPa, an additional metastable phase known as the  $\omega$ -phase forms. This phase can also be formed by quenching alloys containing certain amounts of beta stabiliser. Currently, this phase has limited industrial significance since ductility is almost completely lost when the precipitates are aged [17].

#### 2.1.1. Fuel cladding degradation mechanisms

Fuel cladding failures compromise both the safety and efficiency of nuclear plant. This is because fuel cladding failure causes water to react with the fuel and fission products to leak into the coolant, causing activation of the coolant. Limits enforced by the nuclear regulators are in place for the maximum allowable coolant activity to ensure personnel safety [18]. Additionally, in most light water reactors, failed fuel must be removed from the core before start-up [18]. The operating limits of reactors, design of assemblies, fabrication processes and metallurgy of cladding are therefore optimised to minimise failure.

During operation of a light water reactor, nuclear fuel cladding is exposed to a flowing aqueous environment and elevated temperature, which makes the cladding susceptible to corrosion. The operating temperatures of the cladding are ~280-320°C for boiling water reactors (BWR), ~290-330°C for pressurised water reactors (PWR) and ~260-310°C for Canadian deuterium-uranium (CANDU) reactors [1,2,4,19]. Operating limits are chosen to ensure failure due to corrosion does not occur under normal operating conditions [18]. However, at burnups higher than the design limit, or where temperature has exceeded normal operating temperature, excessive corrosion can lead to failure [18]. Since zirconium oxide has a lower thermal conductivity than zirconium metal, a thick oxide film can cause local temperature to increase and combined with oxide spalling can lead to cladding perforations [20].

During the corrosion process, zirconium alloys pick up hydrogen, which is precipitated as hydrides when the concentration is above the solubility limit [3]. Since mechanical properties can be adversely affected by the presence of hydrides, limits on maximum allowable hydrogen concentration are in place by reactor operators [21]. Further understanding of the hydrogen pickup process, to reduce the amount of hydrogen that enters the metal compared to the amount produced during corrosion (known as the hydrogen pickup fraction) has therefore been a focus of recent alloy development. Additionally, hydrides enable the delayed hydride cracking mechanism, a sub-critical crack initiation and growth mechanism.

Mechanical interaction between the fuel pellets and the cladding, as a result of fuel pellet swelling during operation, is known as pellet cladding interaction (PCI). In the presence of aggressive fission products such as iodine, failure due to iodine-induced stress corrosion cracking (I-SCC) can then occur. Dimensional changes of cladding can also occur as a result of creep (a time-dependant thermally- and irradiation-enhanced process which occurs due to an applied stress below the yield stress) and irradiation growth (which occurs in the absence of stress) are also influenced by texture, as well as grain size, dislocation density and alloying content [22]. This can cause bowing of entire fuel assemblies, interfering with control rod motion [23]. As well as causing irradiation growth, neutron radiation also causes irradiation hardening, which increases the yield stress and decreases ductility of the material as a function of fluence [24], accelerates corrosion and hydrogen pick-up [3,20] and increases the susceptibility of cladding to I-SCC. Therefore, to achieve a full understanding of cladding performance, irradiation should be considered.

#### 2.1.2. Commercial alloys

The composition of commercial zirconium alloys has been modified as the impact of alloying elements on material properties and degradation mechanisms have been better understood. Although pure zirconium was first used in naval nuclear reactors, it was found that by adding tin, corrosion rate in early stages could be improved whilst retaining a low neutron absorption cross-section [1]. This binary alloy became known as Zircaloy-1 (Zr-2.5wt%Sn), the first in the Zircaloy family of alloy developments. However, long term studies showed corrosion was not significantly better than pure zirconium [1]. It was later determined that tin stabilises the  $\alpha$ -phase in supersaturated solid solution and at concentrations above 0.5 wt% contributes to solid solution strengthening, at the expense of corrosion resistance [25]. The development of the next alloy came about as a result of accidental contamination of Zircaloy-1 with stainless steel [2]. It was found that addition of iron, chromium and nickel and a small reduction in tin was beneficial to corrosion resistance [20]. This new alloy was named Zircaloy-2 (composition is shown in Table 2.1) and is still used in BWRs.

Alloy	N	Mean nominal composition (wt %)				
	Nb	Sn	Fe	Cr	Ni	
Zircaloy-2	_	1.50	0.12	0.10	0.05	
Zircaloy-4	_	1.50	0.20	0.10	—	
Zr-2.5Nb	2.50	—	—	—	—	
ZIRLO	1.00	1.00	0.10	—	—	
Optimised ZIRLO	1.00	0.70	0.10	—	—	
M5	1.00	—	0.05	0.02	—	

Fable 2.1. Commercia	ly important zirconium	alloy compositions.	[1,6,20]
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The tin content was further reduced in the next iteration, due to its detrimental effect on corrosion resistance with increasing core lifetimes. This alloy was known as Zircaloy-3, but poor mechanical and creep properties lead to its abandonment [20]. Certain alloying elements also have a significant impact on the hydrogen pickup fraction in the material. Nickel was removed for this reason in Zircaloy-4 and has not been included in any of the niobium containing alloys [20]. Small amounts of oxygen are added, as even a small amount increases the yield strength of the material. Usually, around 0.1 wt% is added which increases yields strength by about 150 MPa at room temperature, at the detriment of total elongation [7].

By adding metals which are more soluble in  $\beta$  than  $\alpha$ , such as niobium, vanadium, iron and chromium, the  $\beta$  phase can be stabilised [6]. An alloy with the addition of 2.5 wt% niobium, called Zr-2.5Nb is used for pressure tubes in the Canadian CANDU reactor [26]. Niobium also improves strength by solid solution strengthening and grain refinement [27]. More recently, ZIRLO and M5 have been developed and have been shown to have improved corrosion resistance and creep performance compared to Zircaloys due to the addition of niobium and reduction of tin and iron [28]. By reducing tin content from 1% to 0.6-0.8%, corrosion performance was further improved in Optimised ZIRLO compared to ZIRLO. Creep strength was decreased as a result of this change but was compensated for by changing the fabrication procedure [20].

#### 2.1.3. Fabrication and microstructure

Large ingots are first produced by melting zirconium sponge together with the required alloying elements in a vacuum furnace. The level of interstitials and impurities, especially hafnium, is carefully controlled at this stage. Hot extrusion and recrystallisation heat treatment are performed to produce a ductile extruded tube (known as 'trex'), with a thickness of 15-20 mm. In the case of niobium containing alloys, a beta quench is carried out at temperatures close to 1050°C to homogenise and extrusion is carried out in the  $\alpha+\beta$ range [2]. It should be noted that modern alloys processed in the  $\alpha+\beta$  range such as ZIRLO and M5 are defined by particular microstructures, as a result of specific heat treatments [2]. For example, M5 is not considered M5 unless given the same proprietary heat treatment as Areva. Niobium-based alloys alloys predominantly contain elongated HCP  $\alpha$ -Zr grain surrounded by a network of metastable BCC  $\beta$ -phase. Successive cold tube reduction is then performed to reach the correct shape, with intermediate annealing steps to restore ductility [6]. Final annealing at 480°C keeps the cold work in the material but relieves internal stresses, leaving the component in a cold work stress relieved (CWSR) state [2,29]. The elongation of grains from the previous cold working process remains. Final annealing at 530-600°C causes complete recrystallisation leaving the component in a fully recrystallised state, with equiaxed grains [29]. Additionally, partially recrystallised microstructures exist when heat treatment is performed at intermediate temperatures [27]. For stressed components such as pressure tubes in CANDUs, material in CWSR condition is typically used as it they have as a higher yield strength due to work hardening [29]. However, material in an fully recrystallised state typically has better creep performance [23].

#### 2.1.4. Second phase particles

Iron, chromium and nickel have very little solubility in the  $\alpha$  phase and they readily form intermetallic phases [6]. For Zircaloys, the most widely reported and predominant are the hexagonal Laves phase, Zr(Fe,Cr)<sub>2</sub> and the tetragonal Zr<sub>2</sub>(Ni,Fe) phase [28]. The size of such particles has been measured using TEM to be 20-600 nm [30–32]. Less commonly, larger

particles of up to 1 µm are observed [30]. In Zircaloy-2, Zr<sub>2</sub>(Ni,Fe) is found in roughly equal quantity to Zr(Fe,Cr)<sub>2</sub> [30]. These nickel-iron type particles have also been found in Zircaloy-4, where nickel is not an alloying element, but impurity levels of nickel can be found [33]. Other particles are also present but are present at a much lower number density [34]. These include Zr<sub>3</sub>Fe binary SPPs, whose formation is sluggish compared to Zr(Fe,Cr)<sub>2</sub>, resulting in a lower number density [2]. The composition, size and volume fraction of these precipitates is thought to play an important role on the corrosion and hydriding behaviour of zirconium alloys under certain conditions [28,35–37]. For Zircaloy-2, material with SPPs in the size range 75 to 120 nm have the lowest corrosion rates in a BWR environment [35]. It has also been shown that increasing SPP volume fraction improves corrosion performance [38]. Slow potential sweep experiments show that the SPPs are more noble than the base metal, however SPPs oxidise quickly when engulfed by the oxide film, leading to porosity and the propagation of cracking in the oxide film around the intermetallic particles [37,39].

In niobium containing alloys, additional niobium-containing particles can be observed (depending on processing parameter), since the solubility of niobium in zirconium is around 0.3-0.5 wt%. [40]. In ZIRLO, hexagonal  $Zr(Fe,Nb)_2$  and cubic  $\beta$ -Nb are most commonly observed [2,28,36]. Complete precipitation of niobium into a uniform distribution of fine  $\beta$ -Nb particles has been found to improve corrosion resistance [36]. As a result, conventionally processed ZIRLO has average  $Zr(Fe,Nb)_2$  and  $\beta$ -Nb particle sizes of around 80 nm and exhibits good in-reactor corrosion performance [28,36]. Coarsening the particles to 200 to 300 nm results in significant deterioration of corrosion performance. In M5, fine (~35 nm)  $\beta$ -Nb particles are observed with a 0.5% volume fraction as a result of processing [32]. Due to the presence of iron, some  $Zr(Fe,Nb)_2$  Laves phase precipitates are also present.

#### 2.1.5. Plastic deformation

Understanding the mechanisms by which zirconium alloys respond to an applied stress, particularly under in-service conditions, is critically important to justify the safety of structural components in nuclear plant. This is because a stress is imparted on the cladding,

which changes through life as a result of PCI and fission gas release. Additionally, the active deformation mechanisms may change during service as a result of irradiation and hydrogen ingress causes brittle hydrides to form [41,42].

Plasticity describes the permanent shape change of a material in response to this applied stress. In a crystalline material, plasticity is generally a result of dislocation motion along crystallographic planes. The crystallographic planes on which dislocation motion can most easily occur are referred to as slip planes, while the direction of shear in a plane is called a slip direction. The combination of a particular slip plane and slip direction is referred to as a slip system [43]. Figure 2.1 illustrates the  $\alpha$ -zirconium HCP cell, which consists of three elementary cells, where the elementary cell is defined by the axial sections  $\langle a_1 \rangle$ ,  $\langle a_2 \rangle$  and  $\langle c \rangle$ . Highlighted are the slip planes which play an important role in the plastic deformation of HCP metals. In the case of all three slip planes, dislocation motion along the close-packed  $\langle 11\overline{2}0 \rangle$  or  $\langle a \rangle$  directions is possible, whereas a Burger's vector of  $\langle 11\overline{2}3 \rangle$  or  $\langle c+a \rangle$  is also possible for the pyramidal slip plane [44]. Slip along the latter was observed in a zirconium single-crystal by Akhtar [45] during compression along the c-axis to 0.2% plastic strain, at temperatures above 800 K. Pyramidal  $\langle c+a \rangle$  slip has also been observed in commercially pure zirconium deformed in tension to 3-6% strain at room temperature [46]. Only limited experimental evidence of pyramidal (a) slip exists [47], however it is sometimes included in models [48].



*Figure 2.1.* Important slip systems for HCP materials including legend and summary of important slip planes and directions.

By measuring the critical resolved shear stress (CRSS), which is the resolved shear stress at which plastic slip begins, the resistance to slip on a given slip system can be measured [49,50]. The resolved shear stress operating on a slip plane in a slip direction is given as:

$$\tau = \frac{F}{A} \mu , \qquad (1)$$

where F is the externally applied force, A is the cross-section of the crystal and  $\mu$  is a geometric parameter known as the Schmid factor, which is given as:

$$\mu = \cos\phi\cos\lambda, \qquad (2)$$

where  $\phi$  is the angle between the normal to the slip plane and the loading direction and  $\lambda$ is the angle between the slip direction and the loading direction. Gong et al. performed micro-cantilever testing on signal crystal cantilevers of commercially pure zirconium with 1000 wppm impurity oxygen, to determine the CRSS values of prismatic (a), basal (a) and pyramidal (c+a) slip systems. By comparing the measured CRSS for micropillar widths from 1 to 10 µm, the macroscopic CRSS values were extrapolated. The results are summarized in Table 2.2 [51]. These measurements suggest that slip in zirconium will occur primarily by glide of dislocations on the  $\{10\overline{1}0\}$  first order prismatic planes along the  $\langle 11\overline{2}0 \rangle$  direction i.e. prismatic  $\langle a \rangle$  slip [51,52]. It should be noted that prismatic slip is also preferred in commercially pure titanium, whereas basal slip is easiest in magnesium [50]. The next most favourable slip mode in zirconium is on the basal  $\{0002\}$  planes with an  $\langle a \rangle$  Burger's vector. To support an arbitrary plastic strain (satisfying von Mises deformation criterion), a shear displacement out of the basal plane is required. To this end, first order pyramidal  $\langle c+a \rangle$  slip is the next most favourable, but it should be noted that the CRSS for this slip system is ~2.5 times larger than the former [51]. This is due to a higher resistance to motion due to the longer  $\langle c+a \rangle$  Burger's vectors compared to  $\langle a \rangle$  [50]. Second order pyramidal  $\langle c+a \rangle$  slip has been observed in magnesium, cadmium and zinc but not in zirconium to the author's knowledge [53].

	Plane	Direction	CRSS (MPa)
Prismatic (a)	$\{10\overline{1}0\}$	$\langle 11\overline{2}0\rangle$	153 ± 30
Basal 〈a〉	<b>{0002}</b>	$\langle 11\overline{2}0\rangle$	204 ± 66
Pyramidal (c+a)	$\{10\overline{1}1\}$	$\langle 11\overline{2}3 \rangle$	532 ± 58

*Table 2.2. Critical resolved shear stress values for pure zirconium with 1000wppm oxygen at room temperature, from* [51].

The CRSS for basal slip has an exponential dependence against temperature, as shown in Figure 2.2a. At reactor operating temperature of 300°C, a CRSS of 50 MPa was measured [54] whilst at a temperature of 600°C, the CRSS of basal slip diminished to around 5 MPa [55]. Slip localisation was promoted at higher temperature and a pronounced slip step was overserved at 623K compared to more diffuse slip at lowers temperatures. This suggests a change in basal <a> slip mechanism with temperature, possibly from multiple closely spaced basal slip traces to single heterogeneous slip and a related increase in strain hardening rate. Prismatic slip remains the easiest slip mode at all temperatures however and exhibits a lower temperature sensitivity than basal slip [55]. Oxygen content also has a significant impact on CRSS, as illustrated in Figure 2.2b, which shows prismatic <a> CRSS at room temperature as a function of oxygen content.



*Figure 2.2. a) Basal <a> CRSS as a function of temperature in Zircaloy-4 and b) prismatic <a> CRSS as a function of oxygen content in commercially pure zirconium. Adapted from* [51,54].

#### 2.1.5.1. Stacking fault energy

Stacking faults are planar defects which occur as a result of an interruption in the stacking sequence of layers of close-packed atoms, either by insertion, removal or shear of an

atomic plane. These faults have an energy associated with them, known as the stacking fault energy (SFE) [56]. Materials with a high SFE cross-slip (where screw dislocations move from one slip plane to another) at low stresses, whereas cross-slip is difficult and twinning is more likely in materials with a low SFE [57]. Therefore, SFE has a significant impact on deformation behaviour. In general, SFE decreases with alloying content and in zirconium alloys, Sastry et al. [58] determined that this energy has a strong dependence with tin content. This is important since many commercially used alloys including the Zircaloy-2, Zircaloy-4 and ZIRLO contain tin. For pure zirconium, the SFE was estimated using dislocation density calculated from X-ray line broadening analysis to be  $240 \pm 50 \text{ mJ m}^{-2}$ [58]. For a Zr alloy with 0.7 wt% Sn, the SFE decreased to  $116 \pm 35$  mJ m<sup>-2</sup> and for an alloy with 3% Sn, an SFE of  $85 \pm 25$  mJ m<sup>-2</sup> was estimated [58]. The values measured should be considered estimates as they are sensitive to the dislocation arrangement parameter, which was assumed by Sastry [58] to be 20. However, they still indicate a qualitative decrease with tin content. It was also noted that the dislocation densities calculated were consistent with those previously measured and the value for pure zirconium is consistent with values determined theoretically and from creep data [59,60]. From the values measured, Zircaloys (which have a tin content of 1.5 wt%) would be expected to have a stacking fault energy at least half that of pure zirconium. Although not experimentally measured, simulations by Pan et al. [61] suggest the effect of niobium on lowering stacking fault energy to be greater than that of tin.

#### 2.1.5.2. Twinning

Apart from pyramidal slip, deformation with a  $\langle c \rangle$  component can also be explained by a process known as twinning [16,50]. This means a portion of the grain volume reorients due to a shear force, leading to co-ordinated individual atom displacements and lattice reorientation [62]. The four most commonly observed twin systems in hcp metals are shown in Figure 2.3. The twinning shear, which is a function of c/a ratio and the twinning system is also given. Equations (1) and (2) used to calculate resolved shear stress for slip also apply for twinning, where  $\phi$  is the angle between the normal to the twinning plane and the external force direction and  $\lambda$  is the angle between the shear direction of twinning and the direction of external force application. Under tensile stress along the direction of

the c axis,  $\{10\overline{1}2\}\langle\overline{1}011\rangle$  twins are activated and less commonly,  $\{11\overline{2}1\}\langle\overline{1}\overline{1}26\rangle$  twins [63]. Under compression in a <c> direction by Akhtar [45],  $\{11\overline{2}2\}\langle\overline{1}\overline{1}23\rangle$  twinning was observed until 800 K and  $\{10\overline{1}1\}\langle\overline{1}012\rangle$  above 800 K [62,64].



**Figure 2.3.** Schematic of modes by which extension twinning (a) and b)) and compression twinning (c) and d)) occur in  $\alpha$ -zirconium. Beneath, plane and direction of twin and twinning shear, s. Adapted from [65].

#### 2.1.6. Anisotropy and texture

The thermal expansion coefficients in zirconium are strongly anisotropic, with the coefficient along the c-axis,  $\alpha_c$  being almost two times greater than the coefficient along a,  $\alpha_a$  (10.8 and 5.5 × 10<sup>-6</sup> K<sup>-1</sup> respectively) [29,66]. This will result in internal stress due to strain incompatibilities following heat treatment [67]. There is also an anisotropy in the modulus of elasticity ( $E_a = 99$  GPa and  $E_c = 125$  GPa) as well as yield strength [16,29]. The slip systems in a hcp crystal are not symmetrically distributed and in combination with the limited number of easy slip systems, a non-random grain orientation is present following thermomechanical processing. This is known as deformation texture and is responsible for the anisotropy of physical and mechanical properties in the bulk material [16]. Texture exhibited following different deformation process is presented in Figure 2.4.

	Defermation	Deformation Deformation		<b>Deformation texture</b>		Annealingtexture	
	process	element	{0002} pole figure	{1010} pole figure	{0002} pole figure	{1010} pole figure	
a)	PilgeringImage: Compared with the second secon	RD AD	AD TD	AD TD	AD TD	AD P P	
b)	$R_W/R_D = 1  \bigcirc \\ \bigcirc  \bigcirc  \bigcirc  \bigcirc  \bigcirc  \bigcirc  \bigcirc  \bigcirc  \bigcirc$	RD AD	AD	D D D	AD	B	
c)	$ R_W/R_D < 1  \otimes  V $	RD AD	AD TD		AD TD		
d)	Sheet rolling	STD SRD	SRD	SRD	SRD STD	SRD	

*Figure 2.4.* Typical deformation and annealing textures of a) pilgered tube, b) tube deformed with equal wall thickness to diameter reduction, c) tube deformed by small wall thickness reduction and large diameter reduction and d) sheet rolling. Adapted from [64].

For pilgering (Figure 2.4a), where thickness reduction  $R_w$  is higher than diameter  $R_d$  reduction, the c-axis aligns at 20-40° away from the tube radial direction, towards the tube transverse direction. The same texture is exhibited during sheet rolling (Figure 2.4d) where the c-axis aligns at  $\pm 20$ -40° away from the sheet normal direction (ND), towards the sheet transverse direction (TD). The Kearns factors (which describe the weighted average of the basal pole figure intensity in the three orthogonal sample directions) are typically 0.05 to 0.15, 0.2 to 0.4 and 0.5 to 0.8 for the axial, transverse and radial directions respectively. Where thickness reduction is smaller than diameter reduction (Figure 2.4c), the basal poles are aligned towards the tube transverse direction, with a  $\pm 20$ -40° tilt towards the tube rolling direction. Where the thickness reduction is equal to the diameter reduction (Figure 2.4b), a hybrid of the previous conditions exists, where the c-axis remains perpendicular to the tube axial direction.

By investigating the texture of zirconium at different stages in sheet rolling, the reasons for this 'split-basal' texture can be determined [64]. Twinning during the early stages of deformation causes the basal poles to orient rapidly towards the sheet ND [68]. This continues until a deformation of about 40% at which point the microstructure is completely twinned [68]. Above 40% deformation, pyramidal  $\langle c + a \rangle$  slip on the  $\{10\overline{1}1\}$  or  $\{11\overline{2}1\}$ planes causes the  $\langle 10\overline{1}0 \rangle$  direction to align with the sheet RD [69]. During recrystallisation annealing, the crystals rotate by around 30° around the c-axis, causing the  $\langle 11\overline{2}0 \rangle$  directions to align parallel to the sheet RD. This causes the  $\{10\overline{1}0\}$  pole figure to rotate by 30° and a slight decrease is observed in the basal pole tilt angle [64,68].

Irradiation growth depends on the material texture, where the degree of growth in a particular direction in recrystallised polycrystalline material is approximately proportional to 1 - 3f, where f is the Kearns factor for a particular direction [70]. This means that for a typical cladding texture with an axial Kearns factor of ~0.05-0.15, there is strong axial growth. However, this is only valid for low fluences and other parameters such as grain size, degree of cold work and tin content also have an effect [71]. Since hydrides precipitate on particular habit planes, texture will also have an impact on the orientation of hydrides and subsequent mechanical properties, which will be discussed in Chapter 2.3.

#### 2.1.7. Impact of texture on mechanical performance

The texture of the material and its relationship to the loading direction will also influence the slip systems activated in the material upon deformation. This is because from a purely geometric point of view, the resolved shear stress on different slip systems depends on loading direction. For example, in grains loaded along the c-axis, twinning and pyramidal <c+a> slip will have the highest resolved shear stress. This is illustrated in Figure 2.5, where Schmid factors are plotted as contours on IPF triangles for Ti-6AI-4V [72]. These plots will differ very slightly for zirconium, which has a different c/a ratio (these are shown later, in Figure 6.9). Where the c-axis is perpendicular to loading (i.e. the right-most side of the IPF triangles in Figure 2.5), prismatic slip is geometrically favourable. To determine which slip systems activate in the material, the CRSS values also need to be considered for each slip system. In a polycrystalline material, the stress state in individual grains will not be the same as the global stress state, an effect which can be considered using crystal plasticity finite element simulation.



**Figure 2.5.** Schmid factor contours plotted on an IPF triangle (where crystal orientations are relative to the loading direction) for a) basal, b) prismatic, c) pyramidal <a>, d) pyramidal <c+a> and e) twinning Schmid factor. Active slip systems determined using SEM at 450°C and 12% strain also plotted. Adapted from [72].

Compression tests on a Zr-1.2wt%Sn sample with similar texture to that represented in Figure 2.4d, show a yield strength (YS) of 352 MPa along RD, 360 MPa along TD and 500 MPa along ND [73]. The YS is lowest in samples compressed along RD, since the texture makes prismatic <a> slip favourable, which has a low CRSS. More twinning was observed when loading in RD as Sn content was increased, which was attributed to an increase in CRSS values for slip as a function of Sn leading to higher flow stress and intergranular strains when plastic deformation begins. Less twinning was observed in the TD sample since fewer grains will have a stress state in the <c> axis, which is required for tensile twinning. Very few grains are in a favourable orientation for easy <a> slip when loading in ND. Very little twinning was observed, suggesting <c+a> slip with a significantly higher CRSS than <a> slip is the principal deformation mode, leading to the higher yield stress observed. For intermediate tin contents of 0.15-0.33 wt%, yield stress increases sharply, consistent with a square root dependence of yield stress on concentration of solute atoms. This correlates well with the drop in SFE as a function of tin content noted by Sastry et al. [58]. This will make the initial barrier to dislocation motion higher, increasing strength and could explain the decrease strain hardening as a function of Sn content measured by Krishna et al. [73]. It should be noted that samples with different tin content also had different grain sizes (which influences strength), oxygen content (which influences strength and CRSS) and different texture.

In Zr-Nb alloys, a similar yield strength increase is observed for increasing niobium content, as is observed for increasing tin content [27]. Due to texture, a difference in 0.2% proof YS is also measured for loading along the different principal directions. For Zr-2.5Nb, a 0.2% proof YS of 525 MPa was measured along the tube axial direction (analogous to RD in sheet materials) compared to 740 MPa along TD, for deformation at room temperature [74]. This is a larger anisotropy than observed for Zr-1.2Sn, the reason for which is not clear. Synchrotron X-ray diffraction was also used to measured slip system activation for the two Zr-2.5Nb samples. For the sample deformed along TD, prismatic slip is activated first followed by basal slip. For the sample deformed along TD, prismatic slip is activated first, followed by basal slip, followed by pyramidal <c+a>. By the end of the test (10% engineering strain), a decrease in {0002} peak intensity along the TD stress direction and an increase in {10-11} along the RD Poisson direction was observed, signifying activation of tensile twinning.

Understanding how mechanical properties and slip system activation changes during service, as a function of neutron fluence and hydride content will be discussed in the next sections. The texture of zirconium alloys allows activation of different slip systems with appropriate loading conditions. Therefore, loading along two or all three principal directions is useful to give an insight into not only easy prismatic slip, but also twinning and pyramidal slip.

#### 2.2. Irradiation damage

During service, zirconium alloys in a nuclear reactor core are exposed to a fast neutron (E > 1 MeV) flux. This results in elastic interactions between the fast neutrons and atoms in the alloy, which get displaced from their initial positions in the crystal lattice [75,76]. The probability of such an interaction occurring is governed by the elastic collision differential cross-section, which is a function of neutron kinetic energy and transferred energy [77]. For a typical fast neutron of 1 MeV, the mean transferred energy to the zirconium atom is around 22 keV [76]. When the transferred energy is sufficiently high, the target atom can escape from its lattice site and is referred to as a primary knocked-on atom (PKA) [75,76]. This atom will then collide with other atoms in the lattice, losing on average half of its
kinetic energy [78]. The collided atom will then interact with other atoms creating a displacement cascade. Following the formation of a cascade, which occurs over a few picoseconds, the cascade is composed of a core with a high vacancy concentration, and self-interstitial atoms at its periphery [76]. Most of the displaced atoms quickly reoccupy lattice sites as a result of elastic recombination or by interaction with a defect sink [75,76]. Of the remaining defects, a significant fraction take the form of clusters as opposed to single interstitials or isolated vacancies [75]. The damage caused to the lattice by irradiation will in turn manifest as hardening, reduction in ductility, dimensional changes and changes in SPP structure, as a function of fluence [6].

#### 2.2.1. Dislocation loops

For neutron irradiation doses lower than  $\sim 5 \times 10^{25}$  n m<sup>-2</sup>, prismatic dislocation loops with an <a> Burger's vector i.e.  $\frac{1}{3}\langle 11\overline{2}0\rangle$  are observed by TEM in commercial zirconium alloys [79]. However, at fluences of below  $\sim 3 \times 10^{23}$  n m<sup>-2</sup> for Zircaloy-2 irradiated at 300°C, the dislocation loops are too small to be measured in TEM (i.e. less than around 2 nm). From this fluence, dislocation density increases linearly with dose in Zircaloy-2 to  $\sim 1 \times 10^{25}$  n  ${
m m}^{-2}$  [79,80]. After this point, it is unclear whether dislocation continues to increase, or if saturation occurs since the quantification of loop size using TEM becomes difficult due to the high density of loops [80]. Loop size increases parabolically to a fluence of  $\sim 1 \times 10^{25}$  n m<sup>-2</sup>, then a decrease in diameter to around 5 nm is observed for Zircaloy-2 irradiated under BWR conditions [76,80]. Irradiation temperature also has a significant impact on both loop size and character (interstitial or vacancy). When irradiated at ~60°C, the dislocation loops in Zircaloy-2 were too small to be seen in TEM and a post-irradiation heat treatment was carried out to determine their character [79,81]. Most, if not all loops were interstitial in nature in this case. For an irradiation temperature of 350°C, the amount of each loop type is approximately equal [79,82]. At this temperature, loops are larger and clearly visible in TEM, with loop diameters of ~10 nm observed in Zircaloy-2 irradiated to  $1 \times 10^{25}$  n m<sup>-2</sup>. When irradiation is conducted at a temperature of ~420°C (above that expected in thirdgeneration PWR or BWR) to the same fluence of  $\sim 1 \times 10^{25}$  n m<sup>-2</sup>, a lower density of larger loops are observed, as illustrated in Figure 2.6a [79]. Primarily vacancy loops are observed at this irradiation temperature [79,83]. As well as increasing in size with irradiation temperature, the number density decreases with irradiation temperature. However in Zircaloy-2, for irradiation temperatures above 500°C, very few large <a> loops are observed to form and above 650°C no damage structure remained [82]. It should be noted that the irradiation temperature dependence of loop character and loop size also depends on alloy composition. For high-purity zirconium with low oxygen, <a> loops are large and low in density compared to Zircaloy-2 irradiated at the same conditions [83]. For niobium containing alloys such as ZIRLO, the increase in <a> loop size with temperature is negligible compared to Zircaloy-2 [84]. However, like Zircaloy-2, no irradiation damage is observed above 650°C [82]. In summary, irradiation-induced <a> loop morphology depends strongly on irradiation temperature, irradiation dose and alloy composition.



**Figure 2.6.** TEM micrographs of dislocation loops in annealed Zircaloy-4 a) after irradiation to  $1.1 \times 10^{25}$  n m<sup>-2</sup> at 700 K in EBR-II. Diffracting vector,  $g = 10\overline{1}1$  and beam direction,  $b = [0\overline{1}11]$ . b) after irradiation to  $8.5 \times 10^{25}$  n m<sup>-2</sup> at 560 K in EBR-II. g = 0002  $b = [1\overline{2}10]$ . Adapted from [79].

At higher neutron fluences, <c> component loops on the basal plane are observed (Figure 2.6b), which have a range of size from about 0.1 to 1.0  $\mu$ m, depending on irradiation temperature [79]. In contrast to <a> loops which can exhibit vacancy or interstitial character, <c> loops are exclusively vacancy in nature with a Burger's vector of 1/6 ( $20\overline{2}3$ ) [81]. In general, there is a correlation between the observation of <c> component loops and accelerated irradiation growth, but their effect on irradiation hardening has not been studied in detail. Partial amorphisation of the Laves phase precipitates in Zircaloys is observed with <c> loops, resulting in the local release of iron into the Zr matrix. This is

thought to cause a finer distribution of <a> and <c> loops which in turn increases the amount of irradiation hardening observed [34,81]. Irradiation also induces formation of niobium and iron-rich nanoclusters of a few nanometres in diameter in Zr-Nb binary alloys [85]. However, since the focus of this thesis is dislocations structures as a result of irradiation, chemistry will not be further discussed.

#### 2.2.2. Mechanical properties

Hashimoto et al. [86] carried out tensile tests at room temperature on high-purity zirconium and Zircaloy-4, irradiated with neutrons at 65 - 100 °C to fluences between  $1.1 \times 10^{21}$  and  $6.3 \times 10^{24}$  n m<sup>-2</sup>. The stress-strain curves are shown in Figure 2.7a and b respectively. Although the loading direction is not specified, the prevalence of prismatic slip suggests deformation along RD [11]. In the case of unirradiated material, pure zirconium has an ultimate tensile strength (UTS) of around 130 MPa, whereas Zircaloy-4 has an UTS of around 440 MPa. The yield stress (YS) was measured to be 50 and 370 MPa respectively. As the radiation dose is increased, the YS and UTS of the material increases, while the elongation to failure decreases [86]. Although the elastic properties of the material do not change as a result of irradiation, the strain hardening behaviour does [87]. For non-irradiated material, the difference between the stress at 0.02% offset and the stress at 0.2% offset is low (around 5 to 30 MPa), whereas after irradiation the difference is between 110 and 185 MPa [87]. This indicates that the strain hardening at the onset of plasticity is larger in irradiated material. Further analysis by Onimus et al. on M5 irradiated with neutrons to  $3.5 \times 10^{25}$  n m<sup>-2</sup>, show that strain hardening rate is two orders of magnitudes higher (at hoop strains of up to 1%), but decreases rapidly (at a higher rate than non-irradiated material) as plastic strain increases [87]. For pure zirconium, a negative work hardening rate at yield was first seen at 0.63 dpa [86]. In the case of Zircaloy-4, a negative work hardening rate at yield was observed from about 0.01 dpa and an increase in magnitude with increasing neutron fluence. For the 0.01 and 0.1 dpa cases in Zircaloy-4, it was noted that there were several bumps in the necking region suggesting multiple necking points [88].



*Figure 2.7.* Engineering stress-strain curve for a) commercially pure zirconium and b) Zircaloy-4 for neutron fluences up to 0.63 and 0.80 dpa respectively. Adapted from [86].



**Figure 2.8.** Deformation mode maps illustrating dose dependence of a) the yield stress and plastic instability stress and b) the total elongation and uniform elongation for zirconium and Zircaloy-4. Adapted from [12].

These same results are also displayed in Figure 2.8a by plotting the yield stress  $\sigma_{YS}$  and true stress at maximum load  $\sigma_{ML}$ , as a function of dose [12]. When the two terms become equal there is no uniform deformation, which occurs at a dose known as the critical dose for necking at yield D<sub>c</sub>, which is ~0.01 dpa for Zircaloy-4 and ~0.1 dpa for Zirconium. Before this point,  $\sigma_{ML}$  is a constant, independent of dose. As well as the data from Figure 2.7, an additional Zircaloy-4 sample was tested up to 24.6 dpa in the LANSCE research reactor. Above D<sub>c</sub>, the true stress at maximum load continues to increase. Figure 2.8b shows the total elongation and uniform elongation of the Zircaloy-4 sample as a function of dose. Dislocation channel deformation was observed from 0.01 dpa onwards, which happens

above a critical dose, D<sub>c</sub>. It should be noted that this is not the case in all materials, especially FCC materials where dislocation channel deformation is exhibited well before D<sub>c</sub> [89].

## 2.2.3. Dislocation channelling

Following deformation of irradiated material, clear bands free or partially-free of irradiation defects are observed in TEM, as shown in Figure 2.9 [41,90]. These provide some explanation to the mechanical property changes exhibited as a result of irradiation. Small radiation-induced defects such as prismatic <a> loops increase the strength of zirconium alloys, since they act as obstacles to dislocation movement, in the same way as forest dislocations [90,91]. Irradiation-induced loops are annihilated or dragged as a result of dislocation glide, when a sufficient stress is applied, in a process known as dislocation channelling which leads to the thin channels cleared or partially cleared of defects [89,92]. If it is assumed that plastic strain occurs only inside channels, which is a reasonable assumption given TEM micrographs, this will lead to softening in the channels as defects are being cleared. This is contrary to a high macroscopic strain hardening rate observed in the early stages of deformation by Onimus et al. [91]. This may be explained by strain incompatibility between channels and the neighbouring grains causing internal stresses and kinematic hardening, counteracting the local softening within channels. The net results will then cause the macroscopic strain hardening rate to be high for low strains. Onimus et al. [91] also suggest that the prominence of basal slip observed in irradiated zirconium alloys deformed along TD will lead to even less compatibility, making the transfer of shear between grains more difficult and exemplifying internal stresses further, since there is only one basal plane compared to three prismatic planes. This also suggests irradiation will change the work hardening behaviour of samples loaded along RD and TD to different extents in the early stages of deformation. The subsequent decrease in strain hardening rate can be explained by the propagation of channels from grain to grain, due to strong stress concentrations at grain boundaries. Eventually, this will lead to specimen scale localisation and may explain the reduction in uniform elongation with irradiation [91].



**Figure 2.9.** a) Propagating basal dislocation channel and b) partially cleared prismatic dislocation channels observed in Zircaloy-4 after tensile testing at 350  $\degree$ C. Adapted from [41].

It has also been shown by Byun et al. [12] that irradiated material has similar deformation characteristics to heavily deformed unirradiated material. Stress-strain curves for irradiated material were superimposed on the unirradiated curve, with an offset in strain. For Zircaloy-4 irradiated to low doses, the stress-strain curves were satisfactorily superimposed on the unirradiated curve [12]. For a damage level of 0.01 dpa, a strain offset of 0.14 was required. If indeed radiation-induced defects and deformation-produced dislocations result in similar net effects of strain hardening, channelling deformation might be observed at high stress, regardless of irradiation. Although dislocation channels have been observed in some materials (Cu, Mo and Al for example), such observations have not yet been made in unirradiated zirconium.

## 2.2.4. Dislocation channel characteristics

Since dislocation glide occurs in certain crystallographic direction, the channels are also formed in certain planes i.e. basal, prismatic or pyramidal. Onimus et al. [41] observed these channels in two Zircaloy-4 sampled irradiated at  $280^{\circ}$ C to  $0.6 \times 10^{25}$  n m<sup>-2</sup> and deformed by ~0.4% in TD, using transmission electron microscopy (Figure 2.9a) and Zr-1Nb irradiated at  $350^{\circ}$ C to  $12 \times 10^{25}$  n m<sup>-2</sup> deformed by 1.6% in RD (Figure 2.9b). When deformed in TD at  $350^{\circ}$ C, only basal channels were observed even in grains with a very high Schmid factor for prismatic slip. Therefore, this suggests that irradiation lowers the CRSS for basal slip to below that for prismatic slip. This was rationalised by Regnard et al.

[47], who showed that the junction created by a <a> dislocation gliding on prismatic plane interacting with an <a> loop was sessile in two cases out of the three possible cases (due to threefold symmetry), whereas the junction created between an  $\langle a \rangle$  loop and a  $\langle a \rangle$ dislocation gliding in the basal plane was always glissile. This may explain why prismatic channels are often found to not be fully cleared of defects, as shown in Figure 2.9b. Regnard et al. also observed basal channelling and some pyramidal channelling in neutron irradiated Zircaloy-4 samples, deformed at 350°C in TD. However, Adamson and Bell [93] reported mainly prismatic and pyramidal channels for deformation along TD at 350°C for an irradiated high oxygen alloy. Farrell et al. [12,89] deformed samples along RD at 350°C and only observed prismatic channels and some pyramidal channels. In summary, it was noted by Onimus et al. [91] that no agreement had been reached and too few observations had been made to have enough confidence in order to produce a predictive model. By investigating deformation in the TD-ND plane (with tensile loading along TD), it was observed that basal channels were connected from grain to grain in 11 out of 17 cases, compared to 2 grains out of 64 with basal channels in RD-TD [41]. This is due to the texture of the material and could induce specimen scale strain localisation which would explain the decrease in uniform elongation with irradiation [41,91].

From TEM images, the mean width and spacing of these channels can also be calculated. Onimus et al. [41] found that the mean width of these channels was between 60 and 80 nm, depending on sample, with a maximum width of 100 nm. Farrell et al. [12,89] found that major channels were 40-75 nm wide and spaced at 0.4-1.1  $\mu$ m, whereas there were relatively few minor bands, <30 nm wide. The spacing and width also decrease as a function of fluence [47]. Simulations by Regnard et al. [94] suggest that the width of the channel stabilises at approximately 10 loop diameters. This is consistent with experimental results, which higher <a> loop density, smaller <a> loop size and therefore narrower dislocation channels as a function of fluence, for the range from 0.6 –3.1 ×10<sup>25</sup> n m<sup>-2</sup>. Onimus et al. [91] also found that as macroscopic plastic strain was increased, so did the mean volume fraction of channels. This is consistent with the observation of increasing channel width as a function of resolved shear strain by Hashimoto et al. [86]. The number of channels per grain was measured to be between 2 and 6. When deformed in RD (Figure 2.9b), only prismatic and pyramidal channels were observed, with channels in 20 out of 41 grains studied. This was attributed to the texture of the material, since only a very low resolved shear stress is present on the basal plane. Prismatic channels had a mean width of 40 nm and a maximum width of 50 nm, with an average of 5 channels per grain.

	Study	Irradiation condition	Number of activated			
	(strain \ temp)		slip/twin systems			
			Pr	Ва	Ру	Tw
RD (axial)	Onimus et al. [41]	12×10 <sup>25</sup> n m <sup>-2</sup> (~20 dpa)	14	0	4	-
	(1.6% \ 350°C)	neutron irradiated Zr-1%Nb				
TD (transverse)	Ungár et al. [95]	Non-irradiated	8	1	6	1
	(15% \ 25°C)					
	Onimus et al. [41]	0.6×10 <sup>25</sup> n m <sup>-2</sup> (~1 dpa)	0	21	0	-
	(0.4% \ 350°C)	neutron irradiated Zircaloy-4				
	Onimus et al. [41]	0.6×10 <sup>25</sup> n m <sup>-2</sup> (~1 dpa)	0	17	0	-
	(0.36% \ 350°C)	neutron irradiated Zircaloy-4				
	Fournier et al. [96]	2 dpa proton irradiated	1	10	0	-
	(0.5% \ 350°C)					

# 2.2.5. Emulation with ion irradiation

The irradiation of samples with neutrons can prove costly, time consuming and logistically complicated [97]. Neutron irradiation of samples carried out in a real power reactor will be subjected to a neutron flux of  $3 - 9 \times 10^{13}$  n cm<sup>-2</sup> s<sup>-1</sup> depending on the reactor [4,98]. In the case of a CANDU pressure tube, end-of-life fluence will be around  $3 \times 10^{22}$  n cm<sup>-2</sup> which is equivalent to around 30 years [98]. In the OSIRIS test reactor in France, fluxes of  $18 \times 10^{13}$  n cm<sup>-2</sup> s<sup>-1</sup> can be achieved, meaning irradiations can be complete five times faster than in a power reactor. Although this is a significant improvement, irradiation experiments can still last many years [75]. An increased neutron flux has also been shown to damage the material more than expected. Pan et al. measured the growth strain in a sample irradiated in the OSIRIS test reactor [98]. Determining the amount of fluence in

a reactor also leads to some uncertainty, which is often quoted as being around 6% [97,98]. Large variations are also present at different areas in a reactor, with the fluence varying by a factor 1.6 in samples placed 20 cm apart [98]. This could pose a problem if a particular neutron fluence was required and makes accurate systematic studies difficult.

Ion-induced irradiation damage has been used extensively as a surrogate for neutron irradiation to investigate the effect of irradiation damage in zirconium alloys [34,80,99,100]. Protons are commonly used, as they have the same mass as a neutron, but a higher displacement rate (by a factor of  $10^2 - 10^3$ ) which means a particular damage level can be reached faster [97]. The irradiated volume in a proton-irradiated sample is confined to a thin region at the surface of the sample on which the beam is incident, leading to very little activation. As a result of the minimal sample activation, handling and performing analysis on such samples can be carried out after 3-7 days, when the short-lived isotopes have decayed [97].

## 2.2.6. Damage calculation

Quantifying the nominal amount of damage caused by neutron irradiation is normally accomplished by quoting the neutron fluence. Since fast neutrons (with energy > 1 MeV) are primarily responsible for atomic displacements which cause irradiation damage, the fluence of only these neutrons is normally quoted. The fluence of other ions used to emulate neutrons is not directly comparable since the particles may be charged (in the case of protons) and\or have different mass (in the case of self-ion irradiation for example). Therefore, the amount of displacements per atom (dpa) is a standard measure of primary radiation damage. Depending on the reactor and therefore neutron energy spectrum, a conversion from neutron fluence to displacements per atom of  $0.5 - 0.6 \times 10^{21}$  n cm<sup>-2</sup> dpa<sup>-1</sup> is applied [34]. An estimation for the number of displaced atoms in an ion cascade can be found using the Kichin-Pease formula, which assumes the following [75,78,101]:

- the cascade is a sequence of two-body elastic hard-sphere collisions;
- a minimum energy transfer (E<sub>d</sub>) is required for displacement, below which no displacements are produced;

- the maximum neutron energy available for transfer is the cut-off energy (E<sub>c</sub>), above which energy losses occur by electronic excitation and ionisation;
- the amount of Frenkel pairs produced has a linear relationship with the initial PKA energy;
- the atoms are randomly distributed, so effects due to crystallinity such as channelling are ignored.

Using a binary collision approximation Monte-Carlo simulation code known as Stopping Range of Ions in Matter (SRIM) [102], the number of displacement per atom (dpa) for a material irradiated with ions can then be calculated. Stoller et al. [101] recommend the use of the quick Kinchin-Pease (K-P) model with lattice binding set to zero. These results most closely matched another reference model known as the NRT model as well as molecular dynamics (MD) models. The full cascade model, which is also offered as an option in the software, showed a significantly larger amount of vacancies, which would lead to inaccurate damage calculations. It was noted that the type of calculation carried out should be noted when dpa values are quoted. The SRIM code outputs vacancies as a function of distance into the material, which therefore allows for dpa to be calculated as a function of depth. Since energy loss is proportional to the inverse square of velocity, the peak in damage occurs near the end of the proton's trajectory, also known as the Bragg peak. The amount of radiation damage produced as a function of distance is shown in Figure 2.10. As energy is increased, the position of the Bragg peak within the material changes from around 10  $\mu$ m at 1 MeV to 55  $\mu$ m at 3 MeV. The plateau region widens and the breadth of the Bragg peak also increases as a function of energy. In order to obtain a wide enough plateau for extracting TEM samples, a proton energy of 2 MeV is commonly used [80,84,103,104].



**Figure 2.10.** SRIM dose profile as a function of depth for protons at energies of 1 MeV, 1.5 MeV, 2 MeV, 2.5 MeV and 3 MeV, being implanted into a 0.23 cm<sup>2</sup> area of zirconium for 6 hours at a current of 15  $\mu$ A.

In order to be displaced from its lattice site, the lattice atom must receive a minimum amount of energy known as the displacement energy [75]. This is not strictly true since in reality the displacement probability is not a step function but is blurred as a result of crystallinity and atomic vibrations [75]. However, this parameter is crucial for the determination of an accurate dose using the Kichin-Pease model. The displacement energy for zirconium has been experimentally measured at around OK using electron irradiation and in-situ electrical resistivity measurement by Neely [105] and Biget et al. [106] to be 21 eV and 24 eV respectively. Griffiths [107] used a high-voltage electron microscope operating at 300K to determine the electron energies required to produce visible dislocation loops. Depending on orientation, a value of between 24 and 27.5 eV was measured. It was noted by Griffiths that measurements obtained at room temperature more closely match the environment in a nuclear reactor. Nonetheless, the displacement energy measured was similar to those at OK. This threshold energy has also been computed by Ackland et al. [108] using molecular dynamics simulations. The minimum value was found to be 27.5 eV (in the basal plane), whilst a maximum value of 130 eV was measured. An average value of 55 eV was determined, but since all orientations were not sampled, this may be an overestimate. The value given in the ASTM E521-16 standard [109] is 40 eV, which is close to the spatial mean obtained by Ackland et al. and this value is therefore used throughout.

## 2.2.7. Comparison of proton with neutron irradiation

To enable the effects of different irradiation species to be compared, a conversion from displacements per atom, calculated for proton irradiation, to neutron fluence of  $0.3 - 0.6 \times 10^{21} \text{ n cm}^{-2} \text{ dpa}^{-1}$  is applied [34]. This depends on the neutron energy spectrum and therefore reactor. For example, for BWR\PWR, the conversion is  $0.6 \times 10^{21} \text{ n cm}^{-2} \text{ dpa}^{-1}$ , whereas for a CANDU reactor it is  $0.4 \times 10^{21} \text{ n cm}^{-2} \text{ dpa}^{-1}$ . Using these conversions, the density and size of <a> loops produced by proton irradiation in zirconium has been shown to be consistent with those produced after neutron irradiation [80,96]. Zu et al. [103] determined similar hardness values from proton and neutron-irradiated Zircaloy-4, at a dose level of ~ 2 dpa. Fournier et al. [96] have also observed dislocation channels in Zircaloy-4 samples, proton irradiated to 2 dpa at 305 °C and deformed by 0.5% in TD at room temperature, similar in width and appearance to those observed by Onimus et al. [41,52,87,91] in neutron irradiated material. Macroscopic localised deformation bands at 45° to the tensile axis were observed in the proton-irradiated region using SEM. As in the neutron irradiated material, the active slip system for deformation along TD was almost exclusively basal.

The increase in loop size as a function of temperature observed during neutron irradiation is also observed during proton irradiation. Topping et al. [84] observed an increase in size, from 10 nm at 280°C to 70 nm at 450 °C for Zircaloy-2. However, due to the high damage rate of protons, a irradiation temperature shift is required to achieve similar diffusion kinetics and therefore comparable radiation-induced microstructural changes [75]. This temperature shift may be different to recreate different features such as dislocation structure, chemical segregation or SPP amorphisation. Topping et al. [84] found that if a similar dislocation structure is required, proton irradiation at 350°C emulates the dislocation structure observed in neutron irradiated Zircaloy-2 from a BWR (temperature 280-330°C), assuming a proton damage rate of around  $1.2 \times 10^{-5}$  dpa s<sup>-1</sup>. For investigating chemical segregation however, a higher temperature shift would be required since back diffusion in material irradiated with protons at 350°C prevents radiation-induced redistribution [103].

Data from zirconium alloys irradiated with neutrons in commercial power reactors is normally at high dpa, after cladding is removed from service. Since data in literature is mostly from proton irradiated zirconium alloys at low dpa, this makes comparison difficult. However, data from material irradiated with neutrons at high flux research reactors exists for lower fluence levels, but may not be fully representative of real in-service conditions. Figure 2.11 shows a comparison of <a> loop diameter and line density for Zircaloys irradiated with protons and neutrons, determined from TEM. Line density generally increases and saturates at high dpa. The loops are too small to see in TEM for very low dpa, increases to around 10 nm at around 5 dpa, then decreases again to 4 nm at around 20 dpa. With the exception of one outlier, the proton and neutron data generally agree. However, studies of the damage structure in Zircaloys irradiated to high dpa (above 15 dpa) do not currently exist for proton irradiation and such a study would be worthwhile.



**Figure 2.11.** Comparison of <a> loop characteristics for proton, commercial neutron and high flux neutron irradiation. a) <a> loop diameter and b) <a> loop line density, as a function of dose, for Zircaloys proton irradiated at ~350 °C, neutron irradiated in commercial reactors at ~280-330 °C and neutron irradiated in high flux research reactors at ~300-350 °C. Data from [76,79,80,84,96,103].

Since dislocation structure is most important for the dislocation channelling mechanism, an irradiation temperature of 350°C will be used throughout this work. This also means that the work performed is consistent with much of the dislocation loop analysis from literature.

## 2.3. Hydrogen effects

The primary source of hydrogen ingress into zirconium alloys during service is by aqueous corrosion with the coolant water. An oxidation reaction dissociates the water into oxygen and hydrogen, according to the simplified ex-reactor corrosion equation [110–112]:

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2 \tag{3}$$

The oxygen combines with zirconium atoms to form an oxide at the metal-oxide interface, whereas the hydrogen can either combine to form hydrogen molecules which are dissolved back into the coolant, or it will diffuse into the metal. The hydrogen pick-up fraction is the amount of hydrogen that enters the metal compared to the amount produced by oxidation [9]. Small amounts of alloying elements (especially Nb) reduce hydrogen pickup rate whereas nickel has a deleterious effect and was removed from Zircaloy-4 for this reason [112]. The hydrogen pickup fraction also varies as a function of exposure time, roughly following the periodicity of oxidation kinetics [111,112]. Factors such as corrosion conditions, microstructure, second phase particle size distribution and irradiation have also been shown to play a role [112]. Typical values for Nb-containing alloys such as Zr-2.5Nb and ZIRLO are 0.02-0.10. For Zr-Fe-Cr alloys, typical values are 0.06-0.25, with Zircaloy-4 in CWSR condition exhibiting a hydrogen pickup fraction of as low as 0.03 [111,112].

#### 2.3.1. Solubility

The terminal solid solubility (TSS) value gives the concentration of hydrogen that can exist in solution at a given temperature. A hysteresis is observed since dissolution occurs at a higher temperature than precipitation. As a result, different curves are obtained for dissolution (TSSd) compared to precipitation (TSSp). Hydrogen contents in excess of the TSSp at a given temperature will precipitate as a zirconium hydride. At room temperature, hydrogen has very little solubility in zirconium and therefore hydrides readily form. The relationship between temperature, *T* and concentration,  $C_{TSS}$  (which can refer to  $C_{TSSd}$  or  $C_{TSSp}$ ) can be described by an Arrhenius-type equation,

$$C_{TSS} = A \exp\left(-\frac{B}{RT}\right),\tag{4}$$

where *A* and Q are constants and *R* is the molar gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>). Experimentally, numerous techniques can be used to measure these constants. The most commonly used are diffusion equilibrium [113–115], dilatometry [116] and differential scanning calorimetry (DSC) [117,118]. McMinn et al. [118] used DSC to calculate TSSp and TSSd curves for for Zircaloy-2 and Zircaloy-4 in various conditions and the data are shown in Figure 2.12. The amount of hydrogen present is measured in weight parts per million (wppm), where 100 wppm is equivalent to 0.01 wt% and therefore 0.897 at%, for pure zirconium. Since the temperature uncertainty of the measurements is  $\pm 2^{\circ}$ C and the uncertainty in the hydrogen content measurements was around 5%, the differences in solubility between the material conditions were noted to be statistically insignificant, in agreement with a study by Kearns [119].



**Figure 2.12.** Plots of TSSp and TSSd for electron beam welded Zircaloy-2 and Zircaloy-4, Zircaloy-2 pressure tube and cold-worked  $\beta$ -quenched Zircaloy-2, adapted from [117].

The solubility curves were fitted with an Arrhenius functional form, although the points at very low hydrogen content (<8 wppm) for the TSSp curve were omitted as they deviated significantly from this form [117]. This may be a result of the formation of the metastable gamma hydride phase, which will be accommodated differently in the matrix and therefore alter the TSSp. The equation for the fits to the solubility data in Figure 2.12 gives the concentration of hydrogen in wppm in the precipitation and dissolution curves respectively to be:

$$C_{TSSP} = 106446.7 \exp\left(-\frac{4328.67}{T}\right),$$
 (5)

$$C_{TSSD} = 138746.0 \exp\left(-\frac{4145.72}{T}\right),$$
 (6)

where T is the absolute temperature in Kelvin. From Figure 2.12, it can be seen that both TSSp and TSSd data for all samples are well fitted by the Arrhenius-type equation. Although this fit is based on data for samples which contain up to 80 wppm, extrapolating up to the 450°C gives values similar to experiments with data in this range. Comparing TSSd and TSSPp curves between many different studies show a variability of  $\pm 10-60$  wppm in the temperature range 160-520°C [114,116,117,119,120]. The TSS values have been shown to be affected by thermal history, the technique used and the heating\cooling rates chosen [117]. These may explain the variability in experimental measurements.

As with CRSS for slip, oxygen also has an effect on hydrogen solubility. Oxygenstrengthened TIG welded Zircaloy-4 showed increased hydrogen solubility and suppressed precipitation and dissolution temperatures due to trapping of hydrogen by oxygen solutes [118]. Irradiation with neutrons to fluences of  $5.5 \times 10^{20} - 1.0 \times 10^{22}$  n cm<sup>-2</sup> at temperatures in the range 250 - 300°C, increase both dissolution and precipitation solubilities compared to non-irradiated material [118]. The hysteresis observed between TSSp and TSSd also grew to 60°C, compared to 40°C for the non-irradiated material. After thermally annealing the samples, the TSS values were measured again and found to have returned to the non-irradiated values. This solubility increase was therefore hypothesised to be due to trapping of hydrogen at irradiation damage sites, specifically <a> and <c> loops, which should no longer be present after annealing.

## 2.3.2. Hydride phases

The hydride phase most commonly observed experimentally, for slow cooling rates (<10 °C/min) and end-of-life hydrogen contents (~400-600 ppm for 6-cycle Zircaloy-4 [121]) in nuclear reactors is the  $\delta$ -hydride [122,123]. This is a face-centred cubic phase with non-stoichiometric room temperature composition ZrH<sub>1.59</sub> where hydrogen atoms randomly occupy a fraction of the tetrahedral sites [9]. The phase is illustrated in Figure 2.13c by

ZrH<sub>1.5</sub>, where six hydrogen atoms occupy the tetrahedral sites. Upon rapid cooling or quenching (faster than ~10 °C/min), a metastable face centred tetragonal phase, γ-hydride with composition ZrH<sub>1.0</sub> and c\a ratio > 1 can also be formed, where hydrogen atoms occupy half the tetrahedral sites, as illustrated in Figure 2.13b [124]. Sidhu et al. [125] used neutron and X-ray diffraction to investigate the phases present in deuterated zirconium for differing deuterium concentrations. For composition from 0-10 at% H, the γ-phase co-exists with  $\alpha$ -Zr, for compositions from 10-50 at% H, both hydride phases co-exist with  $\alpha$ -Zr, for 50-60 at% H only the  $\gamma$  and  $\delta$ -phase are present and for a narrow composition range 60-62 at% H, only the  $\delta$ -phase is present. Barraclough and Beevers [126] noted that homogeneous grains of  $\delta$ -hydride were produced in the composition range ZrH<sub>1.61</sub> to ZrH<sub>1.66</sub>. This corresponds to 61.7-62.4 at%, which is in agreement with neutron diffraction experiments by Sidhu et al. [125]. When  $\delta$ - and  $\gamma$ -hydrides are be present simultaneously,  $\gamma$ -hydrides are normally observed as being embedded in a  $\delta$ -hydride blister or at the tip of  $\delta$ -hydrides [127].



**Figure 2.13.** Relaxed crystalline structures of a)  $\alpha$ -zirconium and three experimentally observed hydrides; b)  $\gamma$ -hydride, c)  $\delta$ -hydride (structure is approximated by ZrH<sub>1.5</sub>) and d)  $\varepsilon$ -hydride. Adapted from [128] with lattice parameters from [124].

At high hydrogen concentrations (> 63 at%), a hydrogen-rich  $\varepsilon$ -phase (ZrH<sub>2</sub>) also exists, which has a face-centered tetragonal structure and c\a ratio < 1 [125]. In this phase, hydrogen occupies all tetrahedral sites, as illustrated in Figure 2.13d. A fourth phase,  $\zeta$ -hydride has also been identified, with a probable stoichiometric formula Zr<sub>2</sub>H. Under TEM observation, the hydrides form small (<500 nm) needle-like precipitates [129]. Since the  $\delta$ 

and  $\gamma$  phases are more commonly observed and implicated in mechanical failures, the majority of experimental studies to date have been on these phases [130].

## 2.3.3. Morphology

All known zirconium hydride phases have a larger unit volume than  $\alpha$ -Zr and therefore a volume expansion is observed during the phase transformation from zirconium to zirconium hydride. Although the FCC delta hydride is crystallographically isotropic, a misfit anisotropy arises from the anisotropy of the zirconium matrix. Carpenter et al. [131] calculated the stress-free transformation strains in  $\alpha$ -Zr as a result of  $\delta$ -hydride precipitation to be 7.20% in the [0001] direction and 4.58% in the [11 $\overline{2}0$ ] and [ $\overline{1}100$ ] directions. The method used for calculation is simple and does not consider alloying or the effect of temperature. Nonetheless, it suggests a platelet morphology for the  $\delta$ -hydride, with isotropic growth in the basal plane, which is observed in TEM [132,133]. For a  $\gamma$ -hydride, a transformation strain of 0.55% was calculated in [11 $\overline{2}0$ ] and almost identical strains of 5.70% and 5.64% along [0001] and [ $\overline{1}100$ ] respectively. This suggests that the  $\gamma$ -hydride precipitates will have a needle-like morphology, which has been observed in TEM [134]. These misfits strains also explain why hydrides align perpendicular to an applied tensile stress, provided it is large enough, since hydride directions with a large positive misfit will nucleate preferentially in the tensile direction [21,135–137].



*Figure 2.14.* a) *High magnification and b) low magnification SEM image of delta hydrides in Zircaloy- 4. Adapted from* [138].

An example of a typical delta hydride morphology in Zircaloy-4 is shown in the low magnification SEM micrograph in Figure 2.14a. Meso-scale delta hydride stringers which

can be over 100 μm in length are observed. On closer inspection with high magnification SEM or TEM, these stringers are composed of many smaller micro-scale hydrides which are less than ~5 μm length are observed, as illustrated in Figure 2.14b. The exact mechanism for the formation of meso-scale hydride stringers is unclear, however it is thought to be associated with sympathetic nucleation i.e. new micro-scale hydrides form near existing ones due to the elastic strain field [138]. With no stress present, hydride stringer typically lie in a radial-transverse direction in Zircaloy plate or circumferential-axial orientation in cladding tubes, as a result of the hydride habit plane and texture, as shown in the optical micrograph in Figure 2.15 [133,135]. However, the reason for the entirely linear alignment is not clear since crystallography would cause the hydride stringer to change orientation across grain boundaries. The presence of smaller micro-scale hydrides is also visible in the optical micrograph Figure 2.15; however, no scale bar was included on the original figure. Although grain size is not specified in this study, it is typically small for Zircaloys and combined with the 2°C/min cooling rate, this gives a heterogenous distribution of hydrides. This is in agreement with a study by Birch et al. [139], in which aligned stringers of hydrides were observed at a cooling rate of >1°C/min in materials with a ~10  $\mu$ m average grain size. Quenching produces a homogenous distribution of hydrides within grains and on grain boundaries. For larger grains (~200 µm), the amount of hydride precipitated on grain boundaries decreases with increasing cooling rate. When cooling at 0.05 °C/min, almost all precipitation is at grain boundaries for the coarse-grained material [139].



*Figure 2.15.* Optical micrograph of TD-RD, RD-ND and TD-ND plane in an electrochemically charged and homogenised Zr-Sn-Nb sample. Adapted from [132].

### 2.3.4. Orientation relationship and habit plane

An orientation relationship describes the favoured crystallographic relationship(s) between a phase (i.e. the FCC delta hydride) and a precursor phase (i.e. HCP alpha zirconium) following a phase transformation. This is important to know, since the orientation relationship has an effect on the nucleation and growth mechanism of hydride precipitates as well as on the mechanical properties of hydrided zirconium alloys. The most commonly observed orientation relationship [124,132,139–146] of delta hydrides in Zircaloys relative to the  $\alpha$ -Zr matrix, precipitated under no stress is:

$$\{0001\}_{\alpha} \parallel \{111\}_{\delta} \qquad \langle 11\overline{2}0\rangle_{\alpha} \parallel \langle 110\rangle_{\delta} \tag{7}$$

This orientation relationship has also been observed by Bradbrook and Lorimer [124] for  $\gamma$ -ZrH in Zricaloy-2. EBSD studies by Une et al. [142,147] found a secondary orientation relationship which was observed for inter-granular stress induced radial hydrides:

$$\{10\overline{1}7\}_{\alpha} \parallel \{111\}_{\delta} \qquad \langle 11\overline{2}0\rangle_{\alpha} \parallel \langle 110\rangle_{\delta} \tag{8}$$

Since the amount of such hydrides is small, only a small fraction of boundaries exhibited that orientation relationship. Kerr et al. [140] observed small amounts (~10%) of an alternative orientation relationship within regions with a high area fraction of hydride, within a hydride blister:

$$\{0001\}_{\alpha} \parallel \{001\}_{\delta} \qquad \langle 11\overline{2}0\rangle_{\alpha} \parallel \langle 110\rangle_{\delta} \tag{9}$$

This was thought to be associated with the accommodation of stresses as a result of the large volume increase due to the high volume fraction of hydride within the blister. Small number of other orientation relationships have also been observed in TEM by Yuan et al. [144] at the edges of hydride platelets and by Perovic et al. [141] on  $\alpha$ - $\beta$  interfaces in Zr-2.5Nb. It was suggested that the stress state caused by the volumetric misfit associated with hydride precipitation lead to the abnormal orientation relationships at the very edges of hydride platelets.

Delta hydrides nucleate on particular habit planes, depending upon the alloy studied. This is important to understand since the circumferential ductility of cladding is particularly affected when the fraction of hydrides aligned in the radial direction is high [21,142]. In

pure Zirconium, a  $\{10\overline{1}0\}$  habit plane is normally observed [123]. Whereas in Zircaloys, the most common habit plane measured is  $\{10\overline{1}7\}$ , which is is 15° away from  $\{0001\}$  [123,124]. Basal habit planes have also been measured, however Kim et al. [146] suggested that this plane may also be observed where the cooling rate is too fast to allow equilibrium conditions (0.5-10 °C/min). Kim et al. [146] also measured the major habit plane for  $\gamma$ -ZrH to be  $\{10\overline{1}7\}$ , which is the same as for the delta hydride. Using the same hydriding technique on both crystal bar zirconium and Zircaloy-4, Westlake found the delta hydride habit planes to be  $\{10\overline{1}0\}$  and  $\{10\overline{1}7\}$  respectively [148]. This means that the texture produced by pilgering (where  $R_w / R_d > 1$  as shown in Figure 2.4a), promotes hydride precipitation roughly aligned with the circumferential direction in Zircaloys.

#### 2.3.5. Mechanical properties and reorientation

Although hydrides precipitate preferentially in the circumferential direction in Zircaloy tubes with a conventional texture, if the hydrogen concentration is high enough, they will still have a detrimental effect on mechanical properties. Furthermore, when a stress is applied during precipitation, such as in dry storage, hydrides can reorient from the circumferential towards the radial direction. Bulk hydride properties will be discussed first, before moving on to hydrides embedded within a zirconium matrix.

Barraclough and Beevers [126] investigated mechanical properties in bulk  $\delta$ -hydride using microindentation. Indentations of the  $\delta$ -hydride regions in a ZrH<sub>1.27</sub> sample gave a hardness value of 265 HV0.05, compared to 112 HV0.05 in the  $\alpha$ -Zr matrix. The same hardness value was observed for hydrides with compositions up to ZrH<sub>1.61</sub>, but in the single phase  $\delta$  region, a drop to 213 HV0.05 was observed. The value drops further in the  $\delta$ - $\epsilon$  region, before becoming approximately independent of concentration at above ZrH<sub>1.77</sub>. Yield strength measurements by Puls et al. [149] show a similar trend to that observed in hardness. Beevers and Barraclough [42] found no deviations from proportionality in the stress\strain curves when a ZrH<sub>1.66</sub> sample (containing only  $\delta$ -hydride) was compressed at temperatures below 100°C. Therefore, it was suggested that no plasticity of  $\delta$ -hydride occurred at room temperature under compression. When tested at higher temperature, small amounts of plasticity were accommodated. By interrupting these tests and performing metallographic

examination, cracks and planar slip lines were observed (Figure 2.16a). From the angle of the slip plane intersection with the sample surface, they were determined to all be of {111} nature. At temperatures above 250°C, the plane could not be measured due to the wavy nature of slip. For samples with coexisting  $\delta$ - and  $\gamma$ -hydrides, the primary role of the  $\gamma$ -hydrides was to inhibit crack propagation (Figure 2.16b).



**Figure 2.16.** a) Slip on {111} planes in  $\delta$ -hydride in ZrH<sub>1.66</sub> sample compressed to 2% strain at 148°C. b) Crack arrested in  $\gamma$ -hydride in ZrH<sub>1.52</sub> sample compressed to 0.5% strain at room temperature. Adapted from [42].

So far, deformation of bulk hydrides in samples with high hydrogen content has been discussed. Even at low concentrations, hydrides in the  $\alpha$ -Zr matrix affect the mechanical properties of cladding, reducing ductility [136,137,150,151]. It has also been shown that the UTS and strain to failure of hydrided zirconium alloys is dependent upon the macroscopic orientation of the hydrides, relative to the tensile direction [21,136,137]. Lee et al. [136] performed ring tensile tests on Zr-0.74Nb-0.7Sn-0.14Fe-0.13O and found that hydrogen charging to 150 wppm caused a small increase in UTS and reduction in strain to failure from ~23% to ~17%. This is consistent with observations by Zhao et al. who measured only a small change in UTS and a halving of elongation to failure with 800 wppm hydrogen for tensile tests along the longitudinal direction of a tube [137]. Hydrides precipitated circumferentially with no external stress (Figure 2.17a), but by applying a circumferential stress of ~68% of the yield stress during cooling, hydrides were reoriented in order to study mechanical properties of radial hydrides [136]. When a load was applied between 573 K and 473K, the reorientation was most pronounced, compared to when a

load was applied at a higher or lower temperature range. For the former case (Figure 2.17c), a significant drop in strength was measured and almost no ductility was observed. In the intermediate cases, where both radial and circumferential hydrides are present, only a small decrease in strength and ductility was measured (Figure 2.17b and d). It should be noted that the larger than expected elastic region in the stress-strain curves in Figure 2.17e is due to the non-standard circumferential test geometry.



*Figure 2.17.* Distribution of hydrides in the radial-circumferential plane a) before reorientation, b)d) after reorientation, applying load at different temperature ranges. e) Stress-strain response of as-received and hydrided samples. Adapted from [136].

Fractography of the samples indicate ductile fracture for the circumferential hydrides (as in the as received material). Where some radial hydrides were present, fracture along the radial hydride was observed. In the material with predominantly radial hydrides, cleavage failure with steps joining brittle cracks along hydride platelets. Cinbiz et al. [135] performed a hydride reorientation experiment of CWSR Zircaloy-4 and showed that a stress biaxiality of 0.57 (such as encountered during pellet clad interaction) reduces the threshold stress to ~110 MPa, compared to ~155 MPa for a sample with no biaxiality. Prior to reorientation, the microscopic hydride platelets are larger, compared to those in the reorientation hydrides. This was also observed by Lee et al. (Figure 2.17) and is consistent with the more difficult growth of hydrides in such orientation.

#### 2.3.6. Hydrogen charging

To investigate the effect of hydrides on material properties, it is necessary to charge specimens with hydrogen. This can be accomplished by corrosion of the sample in an autoclave, but this process takes a long time to generate end-of-life hydrogen concentrations. Gaseous charging and cathodic charging are two methods that have been used in literature to achieve a faster rate of hydriding.

Gaseous charging has been used extensively to produce hydride samples [152–155]. In this technique, the specimen is brought into contact with hydrogen gas at high temperature [152]. This has the advantage of producing a reasonably uniform hydrogen concentration in one step. To minimise any microstructural changes, charging should be carried out below stress relief temperature (480-595°C) [152]. Oxygen is detrimental to hydrogen pick up rate and as a result, multiple flushing cycles with Argon are often carried out prior to charging [152]. Pickling the sample in an acidic solution of 10 mL HF, 45 mL HNO3, and 10 mL distilled water for 2 minutes to remove the native oxide layer has also been proposed [153]. The hydrogen content dissolved in the alloy can be controlled by measuring the partial pressure of hydrogen gas in the charging chamber. Sievert's law gives the hydrogen content expressed as an atomic ratio,  $C_H$  as:

$$C_H = K_H P_{H_2}^{1/2} , (10)$$

where  $P_{H_2}$  is the equilibrium hydrogen pressure in pascals and  $K_H$  is the Sieverts constant [156]. Yamanaka et al. [156] summarise literature which have calculated Sieverts constant as a function of temperature.

An increase in hydrogen concentration was measured for hydrogen partial pressured up to 7.6 MPa by J.-H Huang and S.-P. Huang [152], above which the TSS of hydrogen was a limiting factor to the concentration reached, at 350°C for an exposure time of 10 hours. The concentration reached in thin tube (0.8 mm) was not found to saturate and was five times larger than in thicker plate geometries for pressures of around 14 MPa. This increased pick up was attributed to the tube having a stress-relieved condition in contrast to the plate which was annealed. Differences in the residual stresses, chemistry and surface-to-volume ratios were also noted. Doubling the exposure time of the sample to the hydrogen gas showed a 70% increase in hydrogen concentration. The gaseous charging technique has also been used by Wang et al. [153], with hydrogen pressures of 1.0 MPa and 2.0 MPa at 450°C for an exposure time of 5 hours, followed by furnace cooling. The

hydrogen concentrations reached were 182 and 1584 wppm respectively. The significant increase in concentration as a function of hydrogen gas pressure was attributed to the square root dependence in the Sieverts equation, discussed previously. On the RD–TD section of the plate, a uniform distribution was observed, but on the ND–TD section a hydride concentration gradient was present.

Owing to the simple experimental apparatus requirements, cathodic charging has been widely used generate zirconium alloys samples containing hydrides to [118,124,132,136,154,157–160]. It requires a DC power supply with accurate current control, materials for an anode and cathode and an electrolyte [161]. Upon application of a current, hydrogen ions are electrochemically evolved from the electrolyte, a fraction of which diffuse into the alloy and the other part is liberated from the surface as hydrogen gas. For low current densities, the hydriding rate is proportional to the current density. Above a critical value, measured to be 100 mA/cm<sup>2</sup> by Sawatzky, the hydriding rate becomes independent of current density and is controlled by diffusion [162].

Ideally, a pickling step should take place prior to charging to remove any surface contamination and oxide from the specimen. This is carried out in a solution of 45% nitric acid, 10% hydrofluoric acid and 45% distilled water [124,157]. It has been shown that hydriding rate is 2-4 times higher in pickled sampled compared to mechanically ground samples [163]. Coating the sample with a ~200 nm nickel layer has been suggested by Cinbiz et al. [135] to reduce oxide formation which impedes hydrogen ingress. The specimen is then used as a cathode in an electrochemical cell. Platinum is normally used as an anode and sulphuric acid is a commonly used electrolyte for low temperature charging. Although charging can be carried out at room temperature, increasing the temperature accelerates the process. Bradbrook et al. [124] used a temperature of 95°C, just below the boiling point of water. Although charging times were not specified, the final hydrogen content in the Zircaloy-2 samples was 70-450 wppm following charging at a current density of 100 mA/cm<sup>2</sup> in 0.5% sulphuric acid. Concentrations of between 0.02M and 1M have been used successfully in other studies, for durations ranging from 3 to 10 days to produce hydrogen concentrations of 70-700 wppm [124,129,132,154,158,159,164,165]. It was noted by Blat

et al. [154] that the hydrogen content introduced by cathodic charging was poorly reproducible.



200 µm

*Figure 2.18.* Optical micrographs of sample a) prior to heat treatment (360 wppm H), b) and c) following heat treatment with 130 wppm H and 400 wppm H respectively. Adapted from [154].

Since the diffusion of hydrogen in zirconium is poor at low temperatures, a thin hydriderich rim is formed on the surface, as shown in Figure 2.18a, for a sample with 360 wppm hydrogen. This was identified using x-ray diffraction by Blat et al. [154] to be  $\delta$ -hydride. More recently however it was determined to be  $\epsilon$ -hydride by Birch et al. [139]. To redistribute the hydrogen throughout the sample, a homogenisation heat treatment is carried out. The temperature should be high enough such that the required hydrogen content is dissolved and the time long enough to ensure the hydrogen diffuses throughout the entire sample. In literature, heat treatments are carried out at temperatures suitable for the amount of hydrogen required in the material (i.e. ~400°C for 200 wppm and ~330°C for 100 wppm) for between 6 and 26 hours, depending on sample size [132,154,161]. Figure 2.18b and c show a cathodically charged sample, heat treated for 26 hours at 430°C then slowly cooled, with 130 and 400 wppm hydrogen respectively. As expected, due to the texture of the tube, the macroscopic hydrides are oriented in the hoop direction. Due to availability of experimental apparatus, cathodic charging will be used in this project to produce hydrided samples.

# 2.4. Strain mapping

Investigating the relationship between microstructure and local strain is crucial to develop an understanding of how features such as grain boundaries, second phases and irradiation induced dislocation loops impact the mechanical properties of materials. Although simple mechanical testing can be combined with microscopy to give qualitative information, this is often unrewarding since features of interest can often cause only very slight changes [166]. Measuring strain localisation in a quantitative manner can be carried out with strain gauges but these provide average strains over large regions. Since microstructural features, such as grains and second phase particles are smaller, methods which can map strain at smaller length scales are necessary [166].

### 2.4.1. Digital Image Correlation (DIC)

Quantitative characterisation of deformation behaviour at the micro-scale is well established using optical microscopy-based digital image correlation (DIC). More recently, the increased spatial resolution of scanning electron microscopy has been exploited to measure strain localisation at the nano-scale [167,168]. This technique is termed SEM-DIC [166,169,170] or high resolution DIC (HRDIC\HR-DIC) [171,172]. Since scanning electron microscopy and powerful computers are common-place in modern laboratories, these studies are becoming more accessible. The ability to generate images over large areas whilst retaining high resolution, by stitching an array of images together, allows sub-grain scale deformation to be studied across a large number of grains [167,173]. Using high-speed EBSD, characterisation of microstructure can be carried out at a similar spatial resolution to DIC measurements in a reasonable amount of time.

The basic principle of the DIC technique is the correlation of unique features which can be identified from images taken at different stages during deformation. By dividing the images into grids containing small sub-regions which contain enough features to unambiguously identify them and calculating the relative displacements of these regions, a displacement vector field can be calculated [166]. Figure 2.19 is a schematic of a speckle pattern image before and after deformation, showing how a correlation index is used to determine the best value for the displacement vector (u, v). Using this method for each sub-region allows a the full-field in-place displacement to be calculated for the region of interest.



*Figure 2.19.* a) Schematic of speckle pattern undergoing an arbitrary deformation and b) determination of displacement vector using a correlation index. Adapted from [166].

By differentiation of the dispalcement field, the components of the in-plane strain tensor can then be calculated using the following relationships:

$$\varepsilon_{xx} = \frac{\partial u}{\partial x}, \ \varepsilon_{yy} = \frac{\partial v}{\partial y}$$
 and  $\varepsilon_{xy} = \frac{\partial u}{\partial y}, \ \varepsilon_{yx} = \frac{\partial v}{\partial x}$  (11) (12) (13) (14)

where (u, v) and (u + du, v + dv) are the two surface displacement vectors located (dx, dy) apart. Since most room temperature deformation occurs by shearing of the lattice [174], it is convenient to plot maximum shear strain, which is given as

$$\gamma_{\rm eff} = \sqrt{\left(\frac{\varepsilon_{xx} - \varepsilon_{yy}}{2}\right)^2 - \varepsilon_{shear}^2} , \qquad (15)$$

where  $\varepsilon_{shear}$  here refers to the average of shear components  $\varepsilon_{xy}$  and  $\varepsilon_{yx}$ . This measure interprets all strains as shear strains and is a good scalar representation of local deformation at sub-micron scale. The ambiguity introduced by the lack of out-of-plane displacement data is also reduced for this reason [167].

### 2.4.2. Patterning

For the DIC technique to work, features must exist on the surface of the sample which enable each interrogation window to be uniquely identified. The finer the pattern, the smaller the interrogation window size which can be used and therefore the higher the resolution of the strain map. In order to achieve reliable strain measurements, the pattern must persist through deformation of the material being studied [175]. The pattern should also be electronically conductive and vacuum compatible in the case of SEM-based DIC. Ideally, the pattern should be non-repetitive, isotropic and have high contrast against the substrate [176].

For some alloys, etching the sample and using the intrinsic microstructural features of the material as a pattern is possible. Although such a technique has not been used on zirconium alloys, it has been successfully used on magnesium alloy AZ31 to measure strain localisation with a spatial resolution of 4 x 4  $\mu$ m<sup>2</sup> [177]. Due to the limited depth of field in optical microscopy, the evolution of topography caused by large strains at triple junctions and surface steps caused decorrelation. Gamma prime precipitates in nickel alloy René 88DT have been more recently exploited as a pattern. Stinville et al. [178] first chemical-mechanically polished the sample surface, before heating to 350°C for several minutes to increase the contrast of the precipitates against the matrix. An SEM was used for imaging and a spatial resolution of 0.4 x 0.4  $\mu$ m<sup>2</sup> was achieved, with a standard deviation strain in the loading direction ( $\varepsilon_{xx}$ ) of 0.2%. This technique is heavily dependent upon the underlying microstructure and due to the lack of features in the zirconium alloy microstructure, specifically no high-volume fraction nanoscale precipitates, it is likely to not be suitable.

Should a pattern using the material's microstructure not be possible or if an etched pattern is too coarse, a pattern can be artificially applied using a number of methods. Gold nanoparticles are commercially available in diameters of 2-250 nm and when drop-cast or spin-coated onto a substrate, provide a high contrast tracking pattern for strain mapping [179]. The applicability of the technique depends on the substrate surface energy, but it has been used successfully by Padilla et al [180] to create a pattern suitable for optical DIC on commercially pure zirconium. Further refinement of the technique has enabled spatial resolutions as high as 0.85 x 0.85  $\mu$ m<sup>2</sup> [170,179,181]. Although this method is fast and inexpensive, aggregation can occur if the sample is not quickly dried [179].

Applying a pattern onto the surface of the sample using lithography or ion-beam assisted deposition is an alternative patterning technique. First, a resist coating is applied, then

exposure from either UV or electrons is used to expose the resist to a pattern. The exposed areas of the resist are dissolved, metal is deposited and the resist coating is removed, leaving the pattern originally exposed [182]. In the case of UV exposure, a mask is used, where speckles are typically made to be around 2-20  $\mu$ m [183]. The pattern can be more carefully controlled in the case of electron exposure, since an SEM or dedicated electron beam writer with accurate beam control can be used, but only a small region of a sample is pattered [182]. This makes the technique unsuitable for strain mapping over larger areas [179]. Grid patterns with a pitch of 2 – 5  $\mu$ m are commonly employed [184,185], but finer random speckle patterns have been used more recently [179].

The vapour-assisted remodelling technique involves passing a vapour over a thin metallic film sputtered onto the surface of material. Using steam as a vapour and gold as a substrate, a fine random speckle pattern has been successfully applied to a number of materials, including titanium [172], steel [186,187] and aluminium [188], achieving submicron resolution strain maps. An entire sample can be patterned with little intervention using this technique. By varying the polishing quality, thickness of the sputtered gold layer and remodelling time, the size and density of the pattern can be manipulated to some extent. Some authors have reported issues with repeatability of this technique however [179]. Speckle patterns used for DIC studies have typical diameters of 40-200 nm and a spatial resolution of 120-160 nm is achieved with an error in strain due to noise of ~0.3 % [168,172,182]. Due to the growth of an oxide layer on the surface of corrosion susceptible alloys such as zirconium and magnesium in a steam environment, the use of this technique does not produce reliable strain maps. In fact, this technique has been used to generate an oxide layer on a zirconium sample on purpose to study the fracture of the oxide layer using in-situ DIC by Platt et al. [189].

More recently, a modified technique utilising a styrene vapour, has been used to generate a random speckle pattern on the surface of an aluminium [183] and magnesium alloy [167]. The sealed system provided by glass remodelling chamber and continuous argon gas flow (illustrated in Figure 2.20) provide an inert environment to minimise oxidation of corrosion susceptible samples. The patterns obtained using this method are typically smaller than for steam remodelling, with a diameter of 20-30 nm [167]. The finer pattern necessitates the use of a smaller horizontal field of view when acquiring images to maintain speckles which are approximately 3 x 3 pixels in size [166]. This means that a smaller area is mapped for a given number of images, but the subsequent DIC spatial resolution obtained is up to 44 nm [167]. The temperatures used for the styrene remodelling process are lower than those used for steam remodelling. Remodelling with steam is carried out at temperatures between 270-300°C for around 3 hours [189], whereas styrene remodelling is typically carried out at around 150°C for a few days to 2 weeks [167].



*Figure 2.20.* Styrene-vapour remodelling apparatus consisting of argon gas (a), which is passed through liquid styrene (b) and flows over a sample heated using an external temperature controller (c) placed inside a sealed glass chamber (d). Taken from [167].

## 2.4.3. Limitations

Since strain maps from the DIC technique are generated by looking at the surface of a sample, the deformation mechanisms encountered may be different to those in the bulk. This is because the surface is unconstrained in the out-of-plane direction on the sample surface. This lack of constraint at the surface can be accounted for by finite element modelling however [190]. Additionally, techniques such as stereo DIC [191] or combining traditional DIC with confocal microscopy [192] can give access to the out of plane displacement. These techniques are generally applied to DIC using optical microscopy however. Assuming the possible theoretical slip directions are known, the 3D slip direction can also be determined from 2D DIC data using a technique known as relative displacement ratio analysis [193] and is straightforward to apply to high resolution SEM-DIC datasets, as discussed in Chapter 3.9.3.

Nonetheless, the prevalence of DIC means comparing the strain localisation exhibited on the surface of different materials is possible, even if the behaviour is not exactly representative of the bulk. This gives an important insight into how different microstructures and materials influence deformation behaviour. It should be noted that the maximum local strains measured using also depend on the interrogation window size (and thus spatial resolution) chosen. Care should be taken when comparing results from different studies and spatial resolutions should always be quoted. Further analysis on this topic will be provided in Chapter 5.1.

The quality of the speckle pattern used for DIC is fundamental to the accuracy of the subsequent strain measurements. For example, a non-isotropic pattern may mean some regions will be more difficult to correlate then others, leading to inaccuracies in the measured displacements. If the magnification or interrogation window size chosen is inappropriate, the spatial resolution or uncertainty in strain will be compromised. Image distortions during the acquisition process can also affect the accuracy of strain measurements. For an SEM, these include image drift, step shifts, spatial distortions and inaccurate calibration of magnification [194]. These can be quantified by taking two subsequent images of an undeformed speckle pattern. Optimal imaging conditions can be determined in the same way by iterating the process for different magnifications, dwell times, beam voltage and current and detector type. This is detailed later in Chapter 3.9.1.

### 2.4.4. DIC studies of zirconium

Maximum local strains in the loading direction of ~ 4 times the applied strain (Figure 2.21a) were reported by Héripré et al. [185], in a recrystallised zirconium grade 702 sample. Lithography was used to apply a gold grid with 2  $\mu$ m spacing and imaging was carried out using an SEM. Strains were measured using a discrete deviation scheme for each 2 x 2 grid, resulting in a spatial resolution of 4  $\mu$ m. An EBSD scan of the same region was taken to determine the Schmid factor for the most likely slip system (Figure 2.21b) and a transformation was applied to superpose the two datasets. It was suggested that high strain regions were located near grain boundaries between grains with a high and a low Schmid factor for prismatic slip (Figure 2.21c), although this does not always appear to be

the case. As well as microscopic heterogeneity, larger strain bands with a characteristic size of 10 times the average grain size were also observed and were aligned at 45° to the loading direction.



*Figure 2.21. a*) *Axial strain field, b*) *Schmid factor for prismatic slip and c*) *superposition of texture and strain data for tensile deformed zirconium. Adapted from* [185].

Elbachiri et al. [195] have also demonstrated similar features in Zircaloy-4 and M5 at characteristic lengths of many times the grain size in the material. In the case of stress relieved Zircaloy-4, this distance was measured to be 2-4 times the grain size and in M5 10-20 times the grain size. This was attributed to the difference in the materials' hardening properties. The strain heterogeneity pattern was shown to appear at the onset of plasticity and remain stable with increasing strain. Little detail is provided about the digital image correlation process but the pattern is stated to be a microgrid. No information is provided about the spatial resolution or the errors associated with the process, making comparisons to other studies difficult. From a histogram of strain data, the maximum Von Mises equivalent local strains reach  $\sim$  1.5-3 times the applied strain for Zircaloy-4, depending on loading direction and amount of applied strain. Less heterogeneity was measured when deforming the sample along the rolling direction.

Padilla et al. [180] utilised 1  $\mu$ m silicon particles to create a pattern suitable for optical DIC on a commercially pure Zr alloy with 50  $\mu$ m grain size. In-situ optical DIC, with a maximum spatial resolution of 50  $\mu$ m, was performed on a sample deformed under uniaxial compression to 1.6% strain. It was noted that speckle pattern was inconsistent and anomalous strain dipoles appeared as a result. Macroscopic deformation bands were

observed at 45° to the loading direction. Maximum local strains of ~ 2-4 times the average strain was measured, depending on loading direction. Strains of up to 4 times were measured when compression was carried out along axis where the crystals c-axes were preferentially oriented due to texture. Strains of up to 2.2 times the mean were measured when compression took place perpendicular to c-axis.

### 2.5. Summary

The impact of irradiation on deformation behaviour in zirconium alloys has traditionally been investigated by analysing stress-strain data and performing TEM. These techniques have provided macroscopic information on ductility and strain hardening as a function of fluence, as well as microscopic dislocation content in grains before and after deformation. Together, this data has led to a robust hypothesis regarding the ductility loss observed due to irradiation. The primary limitation of TEM however is that sample preparation is destructive and only a limited area can be investigated. DIC is a complementary technique which allows accumulated strain to be measured non-destructively during deformation on a mesoscopic scale at sub-micron resolution.

Although strain localisation studies using DIC have been carried out on non-irradiated zirconium alloys [180,185,195], they have focussed on deformation on the grain scale. Developments in patterning have enabled higher resolution studies of other materials, such as magnesium and titanium, which allow a large amount of additional information, such as slip system activity, shear band continuity and localisation around second phase particles to be determined. Therefore, it is hoped that HRDIC and EBSD in an SEM can be applied to study the effect of irradiation on strain localisation and slip system activity in commercial zirconium alloys. Since zirconium hydrides also have an impact on the mechanical properties of zirconium alloys, they will also be studied using the same techniques.

## 3. Experimental methods

This section first describes the material used in the subsequent studies. The methods used to emulate in-reactor degradation, namely proton irradiation and hydrogen charging are given next. Analysis techniques used to characterise the material and its subsequent deformation are then described. Finally, a schematic summary of the entire strain mapping workflow is given. All experiments were carried out at the University of Manchester, with the exception of the proton irradiation which was carried out at the Dalton Cumbrian Facility.

## 3.1. Material

The first alloy studied was ZIRLO<sup>TM</sup> (Zr-1.0Nb-1.0Sn-0.2Fe) provided by Westinghouse in the form of 0.7 mm thick sheet. The grains in this material are equiaxed with a mean diameter of ~3  $\mu$ m as illustrated in Figure 3.1a. Zircaloy-4 (Zr-1.5Sn-0.2Fe-0.1Cr) was also provided by Rolls-Royce in the form of 5 mm plate. The grains in this material are also equiaxed, but with a mean diameter of ~9  $\mu$ m as illustrated in Figure 3.1b. Both materials have a similar texture, where the c-axis of the crystal is preferentially oriented in ND and split in TD. In the case of Zircaloy-4, this split is ±26° towards TD and in ZIRLO is ±24° towards TD. The Kearns factors of the basal pole figure intensity with respect to the sample RD, TD and ND are f<sub>R</sub>=0.1, f<sub>T</sub>=0.2, f<sub>N</sub>=0.7 respectively for both materials. Specimens for tensile testing were prepared by electrical discharge machining (EDM).





*Figure 3.1.* Optical micrograph using a differential interference contrast prism for a) Zircaloy-4 and *b*) ZIRLO, showing the grain structure of each material.

# 3.2. Sample preparation

Prior to the commencement of any sample analysis, the surface must be polished to remove any surface roughness. This is particularly important for EBSD, since diffraction only occurs from the top  $\sim$ 50 nm of the specimen [196]. The sample preparation procedure followed for the zirconium alloys used in this study was as follows:

- Manual polishing to 800 grit until the sample is flat and scratches all are uniform in direction and size, which usually takes around 20 seconds, depending on initial sample flatness.
- Polishing with 6-micron diamond paste on MetPrep PA-W cloth for 15 minutes, rotating the sample in the opposite direction to the wheel motion at about 120 Hz and checking every 5 minutes using an optical microscope until the scratches are randomly oriented and uniform.
- Polishing with 1-micron diamond polishing compound on MetPrep Alphacloth M for around 10 seconds and then checking every 5 seconds until scratches are not visible at 20x magnification on an optical microscope.
- Polishing with a 4:1 solution of OPS:H<sub>2</sub>O<sub>2</sub> on MetPrep TrueNoire M for about 30 minutes, rotating the sample in the opposite direction to wheel motion at about 120 Hz, then checking every 15 minutes using polarising microscopy. Water was applied to the wheel for the final minute of polishing to ensure all the OPS was removed.

The sample was thoroughly cleaned between each step to avoid contamination of polishing cloths.


**Figure 3.2.** Bright-field images following a) grinding, b) 6  $\mu$ m polishing and c) 1  $\mu$ m polishing. d) Differential interference contrast image following final OPS step.

A Zeiss Axio Scope.A1 was used to perform optical analysis of specimens. Bright field imaging of samples was used in the early stages of sample preparation to identify uniformity, direction and intensity of scratches. The intensity decreases as polishing steps progress as shown in Figure 3.2a-c. Dark field imaging was used after sample preparation to identify any remaining scratches which could later compromise EBSD Kikuchi pattern quality. The visibility of grains using differential interference contrast as shown in Figure 3.2d indicates the sample has been prepared to an adequate standard for SEM microscopy and EBSD analysis.

#### 3.3. Proton irradiation

Irradiation of specimens was carried out at the Dalton Cumbrian Facility's 5 MV Tandem Pelletron Ion Accelerator [197,198]. A toroidal volume ion source is used to produce a high flux of H<sup>+</sup> ions, which are then passed through a Rubidium charge exchange cell to produce H<sup>-</sup> ions. The beam is then extracted and pre-accelerated before being accelerated by the pelletron to a selected beam energy. In this case 2 MeV was chosen to ensure an adequate penetration depth whilst also permitting a high enough flux to complete the irradiations in a reasonable time. The negative ions pass through an argon gas stripper to convert the H<sup>-</sup> ions into protons. The protons then travel through the high energy beamline to the target station, which is held at a vacuum of  $5 \times 10^{-6}$  Torr or better. Prior to the sample stage, water cooled tantalum slits are placed to control the extent of the irradiated area. To ensure a hard edge, the beam is over-scanned by one beam width onto the vanes of the slits.

In order to allow for accurate temperature control and fast cooling of the stage after irradiation to minimise annealing out of the irradiation damage, a combination of cooling plate and ceramic heater are employed at the base of the stage shown in Figure 3.3a. Between these components and the sample, a steel plate with rectangular cut-out containing Indium (melting point 156°C) is used to provide good thermal contact due to its high thermal conductivity in the liquid state. The size of this indium bath should be larger than the area to be irradiated so that the temperature across the entire irradiated area is consistent. To ensure the indium fills the gap in the steel fully, prior to every sample change, it is melted while the stage is vertical and made flat against the surface of the steel. After the indium has cooled, the samples are clamped in place using a steel shim. Aluminium foil is placed between the shim and samples to encourage good contact for samples of differing thicknesses. Spacers of the same material and thickness as the samples to be irradiated are placed on either side (Figure 3.3b) to ensure the indium bath is fully covered. The beam is rastered over the spacers to ensure the entire width of the samples is irradiated. A tantalum shield is placed on top to reduce incidental activation from the beam. Prior to evacuating the chamber, a leak test is performed by heating the indium above its melting temperature using the heaters.



*Figure 3.3. Irradiation stage at the Dalton Cumbrian Facility as viewed a) from the side and b) from the direction of the beam (without clamp and tantalum shield).* 

The beam is aligned using quartz slides placed around the area to be irradiated and mounted above the tantalum shim. A marker pen is used to place fiducials on the slides denoting the target irradiation area. When the beam is incident upon them, the quartz fluoresces and the marker is visible as a dark line. Initially a lower beam energy is used, such as to not start causing irradiation damage and the slits are all opened and the beam is over-rastered. The slits in the x direction are moved to produce a beam of the correct width (as determined by the fiducials created by the marker pen) and the positions noted. Then, the slits are all opened again and this time the slits in the y direction are moved to produce a beam of the correct beam.

#### 3.3.1. Damage depth calculations

The theoretical penetration depth distribution of the protons was calculated using SRIM 2015. A 40  $\mu$ m layer of zirconium was created into which Hydrogen ions are incident at 0°. As recommended by Stoller et al [101], a quick Kinchin-Pease calculation in SRIM is used as it was found to be more accurate. The lattice binding energy was set to 0 eV and the threshold displacement energy was set to 40 eV as recommended by ASTM [109]. The total number of vacancies generated is calculated and output as a function of sample depth. In order to calculate the displacements per atom (dpa), the following equations were used:

dpa 
$$\begin{bmatrix} \text{disp.}/_{\text{atom}} \end{bmatrix} = \frac{\text{SRIM output} \begin{bmatrix} \text{disp.}/_{\text{Å ion}} \end{bmatrix} \times \text{fluence} \begin{bmatrix} \text{ions}/_{\text{cm}^2} \end{bmatrix} \times 10^8 \begin{bmatrix} \text{Å}/_{\text{cm}} \end{bmatrix}}{N_t \begin{bmatrix} \text{atom}/_{\text{cm}^3} \end{bmatrix}}$$
(1)

Fluence 
$$\left[\frac{\text{ions}}{\text{cm}^2}\right] = \frac{\text{current } [A] \times \text{time } [s] \times 6.242 \times 10^{18} \left[\frac{\text{ion}}{\text{c}}\right]}{\text{area } [\text{cm}^2]}$$
 (2)

Figure 3.4 shows a plot of dpa as a function of penetration depth for 2 MeV protons incident upon an area of 0.24 cm<sup>2</sup> for one hour. This Bragg peak, whose position is constant for a given beam energy, occurs at around 30  $\mu$ m in this case.



Figure 3.4. Plot of displacement per atom against depth for 2 MeV protons in Zircaloy-4.

This dose in a sample is often quoted at 60% of the modal depth and in this case is 0.16 dpa. The output from these calculations are used to decide upon the target damage levels for the samples, which is a function of beam current, irradiated area and time.

## 3.3.2. Temperature control

Due to the increased damage rate of proton irradiation compared to neutron irradiation, Was et al. [75] suggest using a higher irradiation temperature to achieve similar diffusion kinetics. In a light water reactor, temperatures of 280 - 340 °C are typical [199] and as a result, a target temperature of 350 °C was chosen for proton irradiation [34]. Temperature monitoring during operation is performed using a thermal camera, mounted at  $30^{\circ}$  to the beam direction. The emissivity is calibrated prior to irradiation by using the heater to increase the temperature of the samples to the irradiation temperature. Thermocouples spot welded on two samples are used to determine the reference temperature. Each sample has a slightly different thickness and emissivity due to sample preparation quality and as a result, the temperature between samples can vary by a few degrees. An average is taken over a line for each sample and an average over all samples is taken to be the irradiation temperature. The sample stage is isolated from the beam line to allow for the current incident upon the samples to be measured.



*Figure 3.5. Example of temperature and current control achievable at the Dalton Cumbrian Facility irradiating five Zircaloy-4 samples to 0.5 dpa.* 

Experimental parameters such as beam current, sample current, temperature, heating current and vacuum are recorded every 2 seconds. An example of the sample temperature and current data gathered during an irradiation experiment is shown in Figure 3.5. Over an irradiation time of 4 hours 39 minutes, the average sample temperature was  $350 \pm 6$  °C and the current on the sample was measured to be  $14.6 \pm 1.1 \mu$ A. The average deviation between maximum and minimum sample temperatures was 4 °C.

The first hour of the data corresponds to the calibration of the thermal camera emissivity by heating the samples using the ceramic heater to the irradiation temperature. Following this, the sample temperature was kept above the melting point of indium. Beam alignment was then carried out with a minimal beam current such that the quartz slide fluoresces (around 1  $\mu$ A). The beam current was then increased to the desired value before increasing the power supplied to the ceramic heater to reach the target temperature for irradiation. The beam causes heating of the sample and any current fluctuation (cause by beam drift for example) will affect the temperature. This can be counteracted by steering the beam to the correct position or manually increasing/decreasing the power supplied to the ceramic heater. After the desired dose level is reached, the heater and beam were simultaneously turned off, whilst retaining the cooling.

# 3.4. Microhardness

In order to accurately identify the width and position on the irradiated region, hardness evaluation was carried out using a Struers Durascan 80 automated microhardness instrument. An array of Vickers indents was placed along the bottom edge of the sample using a 0.05 HV load and a spacing of 250 µm, as shown in Figure 3.6b. Given that opposing indenter faces are at 136°, the indents have a depth of 1/7 times their diameter. Therefore, in this case, the depth of the indentation is around 3 µm. This is enough to overcome any surface effects such as sample preparation and proton sputtering. Since the plastic zone ahead of a Vickers indent is around 5-10 times indent depth, the majority, if not all of this zone is within the plateau of the proton penetration curve. Using these indentation conditions, the irradiated region shows a clear increase in hardness, as illustrated in Figure 3.6. The error bars in this graph were determined by taking the standard deviation of the hardness values of 20 indents placed in the non-irradiated region. Another indent is placed 250 µm above the centre of the region, then smaller indents are placed near the centre of the sample to act as fiducials for subsequent orientation mapping and HRDIC studies. The same indent pattern is also placed in the non-irradiated region for the same purpose. Following microhardness testing, the samples were polished with a 4:1 solution of OPS:H<sub>2</sub>O<sub>2</sub> to remove any oxidation.



*Figure 3.6.* Optical micrographs of the a) centre and b) edge of the sample, with corresponding Vickers hardness plot on a sample irradiated to 0.15 dpa.

## 3.5. Hydrogen charging

To produce samples with hydrides, similar to those observed in-reactor, electrochemical hydrogen charging followed by a redistribution heat treatment was performed. Prior to this, each sample was pickled in a solution of 10% hydrofluoric acid, 45% nitric acid and 45% distilled water for a minute, to remove the oxide on the surface of the specimen. The pickling process was interrupted by dipping the sample in a large beaker of water and then cleaning thoroughly with ethanol. The sample geometry was measured using callipers and was then spot welded to pure zirconium wire before being connected to the negative terminal of a power supply. Two platinum electrodes were used as anodes and were connected to the positive terminal of the power supply. The electrolyte used was 1N sulphuric acid, created by diluting high purity (95%+) sulphuric acid with distilled water.



*Figure 3.7.* a) Schematic and b) image of the equipment used to electrochemically hydrogen charge zirconium samples.

Using the dimensions measured earlier, the area of the sample exposed to the acid was calculated and multiplied by the chosen current density. This value was programmed into the power supply before being turned on. During the cathodic charging process, bubbles of hydrogen gas were seen leaving the sample as a result of electrolysis. Following hydrogen charging, the samples were homogenised in a furnace with an Argon environment at 400°C for 18 hours, before being furnace cooled at 2 °C/min to promote the formation of  $\delta$ -hydrides. The sample was subsequently ground and polished prior to further analysis

## **3.6.** Styrene-vapour assisted gold remodelling

Styrene-vapour assisted gold remodelling was the technique used to apply a speckle pattern to the surface of the sample for HRDIC purposes, as this patterning technique is suitable for producing samples on materials susceptible to oxide formation. Previous development of similar speckle patterns on zirconium alloys was performed in a water vaporisation environment and the HRDIC analysis indicated oxide cracking, which masked the deformation behaviour of the underlying microstructure. Another important advantage of remodelling in styrene is that the remodelling is typically performed at lower temperatures than the water with the temperature ranging from 100-200°C compared to 300°C. This is beneficial when investigating the effect of irradiation damage, as the remodelling is performed post irradiation and therefore reducing the remodelling temperature is critical in ensuring that the irradiation damage is not annealed out and that the deformation structure is not changed. Following a 5 hour heat treatment at 200°C,

Topping et al. [84] showed no significant change in <a> loop density. Figure 3.8 shows the experimental arrangement used to perform remodelling of a thin gold film in a styrene environment. Prior to the polished samples' placement in this apparatus, a uniform gold layer was sputtered onto the surface using an Edwards S150B sputter coater. The sputtering rate of the equipment is 5-8 nm/min and a sputtering time of 3 minutes was used for this study. By altering the gas admit flow rate, a pressure of  $\sim 5 \times 10^{-1}$  atm was used and a sputtering current of around 0.4 mA.



Figure 3.8. Schematic of the equipment used for styrene-assisted remodelling of a thin gold film.

Argon gas is passed through liquid styrene with a flow rate which can be varied using the control on the bottle and monitored with an analogue flow meter. The samples are heated on a hot plate, which is connected to an external temperature controller. By exposing the samples to the styrene vapour, the gold layer changes from a uniform layer to a discontinuous pattern, by a process of dewetting [200]. Assuming sample preparation is consistent, as this will impact the ability of the gold to dewet, the important parameters are the argon flow rate, sample temperature, remodelling time and the thickness of the initial gold layer. By changing the parameters, the morphology of the gold can be optimised to provide a pattern suitable for application of DIC. To prevent oxidation of the samples during remodelling, the chamber was purged with the argon-styrene mixture at room temperature before any heat was applied to the sample.

# 3.7. Mechanical testing

Microtensile samples (geometry in Figure 3.9) were deformed in uniaxial tension with a Kammrath-Weiss microtester equipped with a 5 kN loadcell. Load and displacement were measured and recorded using DDS software on a laptop connected to the microtester. The sample was placed as straight as possible in the microtester before being firmly clamped using bolted grips. The crosshead displacement rate used throughout was 5  $\mu$ m/sec, which corresponds to an initial strain rate of  $1.7 \times 10^{-4}$  sec<sup>-1</sup>.



Figure 3.9. Microtensile sample geometry. Units in mm.

# 3.8. Scanning Electron Microscopy (SEM)

Imaging for the subsequent digital image correlation experiment was carried out on an FEI Magellan HRFEG-SEM. Since the gold speckles and zirconium substrate have different atomic numbers, 79 and 40 respectively, backscatter electron (BSE) imaging was used to provide contrast. This is because the number of backscatter electrons increases proportionally to atomic number [201]. Backscattered electron imaging is less sensitive to topographic features and surface contamination of the sample then secondary electron imaging. This is important because out-of-plane slip can give rise to sharp topographic features, which would later be interpreted as a rogue pattern [187]. The type of detector chosen was a concentric backscatter detector (CBS) which allows for angle selectivity, although in this case, all rings were active to improve signal. In order to resolve the speckle pattern with high resolution, immersion mode was utilised. In this mode, the objective lens generates a magnetic field that extends to the sample to improve resolution [202]. To

collimate electrons towards the detector and to collect high-angle BSE, a stage bias was applied [203]. Figure 3.10 illustrates the impact of stage bias and immersion mode on attainable image quality. The beam was re-aligned and focused as well as possible before the acquisition of each image.



**Figure 3.10.** BSE images using a) field-free mode, b) field-free mode with stage bias and c) immersion mode with stage bias of a representative gold speckle pattern on a Zircaloy-4 sample. The same particle is identified in each image by an arrow and the same region by a circle.

In field-free mode, the speckles cannot be clearly resolved, even with a stage bias. By enabling the magnetic immersion lens, clearly defined speckles can be seen with high contrast. Immersion mode also provides additional contrast in regions where speckles are difficult to see in field-free mode (such as the circled are in Figure 3.10). These images were taken at identical conditions to those used for DIC. The magnification was chosen to give speckles of around 3 pixels in diameter. The imaging parameters for DIC are summarised in Table 3.1. In order to maintain a high spatial resolution, but also map a statistically significant number of grains, FEI Maps [204] was used to produce a montage of images. An overlap of 15% was chosen to ensure sufficient area for an accurate translation offset calculation. Between each frame, a delay of 5 seconds was used to allow vibration from stage movement to subside.

Imaging Mode	BSE
Detector	CBS
Accelerating voltage (kV)	5
Stage bias (kV)	2
Beam Current (nA)	0.8

<b>Table 3.1.</b> SEM beam a	and scan parameters	for DIC image	acquisition.
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Lens modeImmersionWorking distance (mm)3.6Dwell (μsec)3Image size (pixels)2048 × 1152Horizontal field of view (μm)10

The 'Grid/Collection Stitching' tool in imageJ [205] was used to create a single large image from the montage acquired from the SEM. It is assumed that all transformations between overlapping tiles are translations and a Fourier transform-based phase correlation method is used to compute translational offsets between tiles. The typical correlation value between images was around 0.9 and was always above 0.8, suggesting a good correlation. Linear blending was used to fuse the images, to minimise the visibility of the seam between images, as this could lead to fictitious strain measurement.

# **3.8.1.** Electron Backscatter Diffraction (EBSD)

Electron backscatter diffraction (EBSD) is a technique carried out using a scanning electron microscope which allows the grain orientation of a crystalline sample to be determined. A stationary electron beam interacts with atoms in a crystalline sample to form a diffraction pattern. These diffracted electrons are captured by a phosphor screen to form an image with Kikuchi bands, which each correspond to a different diffracting crystal plane. In order to maximise the intensity of backscattered electrons, the sample stage is tilted to 70°. The diffracted signal containing the Kikuchi bands is collected by a CCD camera. Assuming the sample geometry is known, the pattern can be related to the crystal structure and orientation in the sample region where it was generated [206]. After performing a background subtraction to improve the visibility of the Kikuchi bands, a Hough transform is applied and indexing algorithms are used to determine the exact crystal orientation and structure at the point. By scanning the beam in a grid over a polycrystalline sample, the crystal orientation can be measured over a large area, resulting in an orientation map.

FEI Sirion and FEI Magellan scanning electron microscopes equipped with Oxford Instruments NordlysMax cameras, connected to a PC running Oxford Instruments Aztec software were used for data collection. A summary of the operating parameters is included in Table 3.2. The region of interest (ROI) on a sample is first located, then the sample is tilted to 70°, moving the stage in the y direction to keep the ROI in the field of view. After applying tilt correction and dynamic focus, the beam is focused and astigmatism corrected with stigmators. The EBSD camera is then inserted and the pattern is checked by pointing the electron beam. At this point a decision must be made about the binning applied to the CCD camera. Higher accuracy is obtained with less binning, compromising speed. This choice also depends on the quality of sample preparation, where a pattern can be obtained from well-prepared samples with large binning. In most cases, the samples are wellprepared and a binning of  $8 \times 8$  is used to give a reasonable orientation error whilst minimising map acquisition time. This gives an indexing rate of around 40 Hz with single frame averaging. The exposure of the CCD camera is optimised automatically and a background collection is performed by scanning the beam across the field of view.

Table 3.2. SEM beam and scan parameters for EBSD.

Microscope	FEI Sirion	Microscope	FEI Magellan
Accelerating voltage (kV)	20	Accelerating voltage (kV)	20
Working distance (mm)	15	Working distance (mm)	11
Spot size	4	Beam current (nA)	3.2

When a correlation between DIC and grain orientation is sought, an EBSD step size of  $0.2 \ \mu m$  or less was chosen. This allows accurate grain boundary maps to be generated and orientation to be studied at the sub-grain scale. For macrotexture measurements, a step size of 2 µm or more was chosen to allow a larger area to be sampled. The typical mean angular deviation for orientation measurements was 0.5° which is likely to be better than the alignment of the sample in the tensile stage and therefore not a limiting factor.

## 3.9. Data analysis

Commercially available software LaVision Davis 8.4 was used to perform the digital image correlation routine. The images at each deformation step were first shift and rotation corrected to remove any rigid-body translation and rotation. Starting with an interrogation window of 1024 x 1024 pixels<sup>2</sup>, a fast fourier transform algorithm was used to calculate the displacement vector field. The correlation was performed at progressively smaller interrogation window sizes, until the desired resolution was achieved. No overlap between the interrogation windows was used. The final pass was performed with a B-spline-6 reconstruction. The data were outputted in the form of a text file. The images from each deformation stage were always compared to the before deformation image rather than using a summation of comparing to the previous step, as this helps to reduce eliminate any errors that may be associated with a particular strain step.

Displacement data from Davis and EBSD data from Oxford Instruments Aztec were read into arrays in Python. By differentiating the displacement data, different components of the strain tensor can be plotted and further analysis carried out. From the EBSD data, grain boundaries can be drawn and misorientation distributions plotted. In order to compare strain data to orientation data, a transformation must be applied to the EBSD data such that it aligns with the data generated from DIC. This is because the EBSD dataset is subject to distortion since it was acquired when the sample was tilted and is also at a different spatial resolution to the DIC dataset. Homologous points in the BSE image (which has some orientation contrast due the polishing process) and the EBSD boundary map were selected. An example of such points is shown in Figure 3.11.



*Figure 3.11.* Homologous points on a) grain boundary map, b) BSE image and c) strain map, used for aligning HRDIC and EBSD data.

Since the BSE image and the resulting strain maps only differ by a scaling factor which depends on the interrogation window size chosen, homologous points for the strain map can be easily calculated. The transform required to transform the EBSD frame to the DIC frame was calculated using an affine transformation (consisting of translation, scaling, rotation and shear) as this adequately aligns the datasets.

## 3.9.1. Error characterisation

To quantify the error in the strain measurements, two successive images were acquired of the same region at the same imaging conditions. Since the sample was not deformed, cross correlating these images gives the distribution of perceived strain as a result of noise and scanning parameters of the SEM. This procedure can be repeated for different imaging conditions i.e. beam voltage, beam current, dwell time or horizontal field width and the error distribution compared.

#### 3.9.1.1. Imaging conditions

The error quantification procedure was carried out for the three imaging conditions illustrated in Figure 3.10, using a (16 x 16) pixel sub-window size, corresponding spatially to 78 x 78 nm<sup>2</sup>, to provide a high spatial resolution (~  $1/100^{\text{th}}$  of the grain size of an average grain). Imaging was carried out using a dwell time of 10  $\mu$ s and one frame was acquired in 36 seconds. The effective shear strain frequency distribution for each condition is plotted in Figure 3.12.



*Figure 3.12.* Frequency distribution of effective shear strain values for a) field-free, b) field-free and stage bias and c) immersion mode and stage bias imaging conditions.

The mean values of effective shear strain for the conditions are 0.31%, 0.32% and 0.18% for field-free, field-free with stage bias and immersion mode with stage bias respectively. The maximum values are 1.26%, 1.25% and 0.69% respectively. Although applying a stage bias does not seem to improve the mean error, immersion mode reduces it by around 80%. Since immersion mode also increases contrast in regions where there appear to be few speckles in field-free mode, the breadth of the error distribution is also reduced, which means maps will have a smaller variation in error. Since effective shear strain is a combination of absolute strain tensor values, the contribution from each is important. For example, in immersion mode, the average values of the absolute in-plane strain tensor components are 0.14%, 0.19%, 0.18% and 0.19% for E<sub>xx</sub>, E<sub>yy</sub> and E<sub>yx</sub> respectively. While E<sub>xx</sub>, E<sub>yy</sub> and E<sub>xy</sub> all exhibit a reasonably random spatial distribution, the E<sub>yy</sub> distribution is banded. This is likely a result of stepping errors when rastering in the y direction.

#### 3.9.1.2. Dwell time

The dwell time sets the amount of time taken for signal collection into the backscatter detector at each of the 2048 x 1768 pixels<sup>2</sup> in an image. Noise is reduced for longer dwell times at the expense of longer image collection time. The mean effective shear strain error for dwell times of 1, 3, 5 and 10  $\mu$ s are shown in Figure 3.13, where the error bars are generated from the standard deviation of the values from a single frame. The error is

halved when increasing the dwell time from 1  $\mu$ s to 3  $\mu$ s, but only decreases by a further 0.05% between 3  $\mu$ s and 10  $\mu$ s. Therefore, a dwell time between 3  $\mu$ s and 10  $\mu$ s range is optimal as the error seems to plateau in this region. Since acquisition time increases linearly with dwell time, the same area can be imaged ~ 3 times faster using a 3  $\mu$ s dwell time as opposed a to 10  $\mu$ s dwell time. Alternatively, an area that is 80% larger can be imaged in the same time. Therefore, the dwell time chosen will be a compromise between minimising error and reducing acquisition time.



**Figure 3.13.** Mean effective shear strain error for dwell times of 1, 3, 5 and 10  $\mu$ s. Error bars are plotted from standard deviation.

#### 3.9.1.3. Image stitching

To assess the effect of stitching on error, two successive 16 x 16 tiles of a patterned sample were collected using immersion mode (with a 10  $\mu$ s dwell time), stitched and cross-correlated. The error magnitude is not significant changed at the stitch boundaries or the overlap regions, as shown in Figure 3.14a. The variation in error increases slightly, with an increase in some cases and a decrease in others. These effects cancel to give approximately the same error in a single frame as in the stitched image. It is significant that the magnitude of the error at these interfaces between images does not significantly increase or have high strain values associated with them, which suggests that there is very little distortion in individual images.



*Figure 3.14. Effective shear strain maps of error characterisation a) across tiles and b) in a single tile where a step image shift has occurred.* 

The most significant source of error in the maps were horizontal artefacts, spanning entire 10  $\mu$ m frames (Figure 3.14b). These result from step image shifts commonly observed at higher magnifications in an SEM [169]. Since they occur at random, there is no way to correct for them after image acquisition. These features were normally 2 pixels in height and over the (16 x 16) tiles used for error characterisation, 8 were observed with an error magnitude greater than 0.5% for the 78 x 78 nm<sup>2</sup> interrogation-window size, corresponding to around 0.3% of the total data points. The maximum error magnitude measured due to an image shift was 1.5%, but the majority have an average value less than 1%. Since they are all horizontal (as opposed to slip bands which are typically at 45°), are infrequent and span entire 10  $\mu$ m frames, they can be distinguished from slip bands in the material.

# 3.9.2. Slip Trace Analysis

By comparing experimental slip trace angles, measured from DIC, with all theoretical slip angles calculated using orientation data obtained from EBSD, the active slip systems can be identified. An example of an effective shear strain map for a single grain in a Zircaloy-4 sample deformed to 2% strain is shown in Figure 3.15a. The slip trace angle(s) are determined using a fast fourier transform (FFT), but this only works in cases where slip bands are not diffuse. In some cases, the angle(s) are determined by hand by drawing lines on three bands and taking an average. In the grain shown in Figure 3.15a, two slip systems are active at 70° and 130° measured counter-clockwise from horizontal. Using grain orientation from EBSD, the intersection of the basal, prismatic and pyramidal slip planes with the sample surface can be determined (Figure 3.15b).



**Figure 3.15.** Schematic of slip the slip trace analysis technique. a) Effective shear map for single grain from a Zircaloy-4 sample deformed to ~2% strain. b) Theoretical slip trace angles calculated from EBSD grain orientation.

By applying an angular acceptance criterion of  $\pm 5^{\circ}$  away from the experimentally measured angle, the active slip system can either be uniquely identified (in the case of slip trace A in Figure 3.15a) or more than one possible slip system identified (in the case of slip trace B). Slip trace A is likely to be of prismatic character, whereas slip trace B lies in between a prismatic and pyramidal plane.

#### **3.9.3.** Relative Displacement Ratio (RDR)

In cases where an ambiguity exists after traditional slip trace analysis, slip direction can be determined using DIC data using a relative displacement ratio (RDR) analysis [193]. This analysis is also useful to determine the Schmid factor of the exact slip system which is active, as opposed to the maximum for all slip directions in a given plane which is normally used. The principle of the technique is to first calculate an experimentally determined value from the strain data, which is a function of slip direction (Figure 3.16a). Then, the value is compared with theoretical values for all possible slip directions (one example is given in Figure 3.16b, but this applies to all possible slip directions).



*Figure 3.16.* a) Schematic for experimental RDR determination from displacement data. b) Schematic for calculating the theoretical RDR for one slip direction.

To do this, slip traces are first identified in a grain from the effective shear strain map (Figure 3.17a) and lines are drawn along them, avoiding the edges of grains. Lines perpendicular to the slip trace, with a length of 3-5 pixels, such that adjacent slip traces are not sampled, are calculated. An example of this is shown in white in Figure 3.17b, overlaid on a map of u displacement. For each line, the u and v displacement values are determined (which correspond to number of pixels displaced in x and in y respectively). The average u displacement,  $u_{av}$  and average v displacement,  $v_{av}$  are subtracted from the respective displacement components to get u-centered and v-centered values. These are plotted for each perpendicular line in Figure 3.17c. Linear regression is performed on u-centered versus v-centered values to determine the experimental RDR. Given the resolution of the strain data, for the five slip traces analysed in the grain lead to over 1200 points on the plot in Figure 3.17c. The R-squared value gives an indication of the quality of the fit, which in this case was 0.88 and, in all cases, analysed, the mean value was 0.94.



**Figure 3.17.** a) Effective shear map for single grain from an irradiated Zircaloy-4 sample deformed to ~2% strain b) u displacement map for slip trace, c) plot of u-centered against v-centered for 253 perpendicular lines and d) possible RDR values (blue) and experimental value (red).

From the grain orientation (determined using EBSD), the theoretical RDR value can be calculated. This is equivalent to the ratio between the x and y components of slip direction in sample coordinates. For the grain in Figure 3.17a, theoretical values between -5 and 5 are plotted in Figure 3.17d. Given the angle of the slip trace, the possible RDR values are shown in bold. In this case, the experimental RDR corresponds to an <a> slip direction.

# 3.10. Overview

The entire deformation analysis workflow is summarised in Figure 3.18. After polishing the sample to EBSD quality, an array of indents is placed to determine the location of the irradiated region (where applicable). Fiducials are then placed in the region(s) of interest to assist with sample alignment. The sample is sputtered with a thin gold layer, prior to being remodelled in a styrene-vapour to change the uniform gold layer into gold speckles, suitable for DIC. Imaging of the region of interest is carried out before deformation and after each deformation step. To investigate a large area, whilst retaining high spatial resolution, automated mapping is carried out. The acquired image tiles are then stitched together and input to the digital image correlation software. Post-deformation EBSD is also acquired then the DIC and EBSD datasets are imported into a Python script to align the datasets and conduct further analysis.



*Figure 3.18.* Schematic of the experimental and analysis workflow for performing deformation analysis.

# 4. Enabling high resolution strain mapping in zirconium alloys

D. Lunt<sup>1</sup>, A. Orozco-Caballero<sup>1,2</sup>, <u>R. Thomas</u><sup>1</sup>, P. Honniball<sup>1,3</sup>, P. Frankel<sup>1</sup>, M. Preuss<sup>1</sup>, J. Quinta da Fonseca<sup>1</sup>

<sup>1</sup> School of Materials, University of Manchester, Manchester, UK.

<sup>2</sup> IMDEA Materials Institute, Madrid, Spain

<sup>3</sup> Rolls-Royce Plc, Derby, UK.

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# **Contribution statement**

The experiment was designed by R. Thomas with assistance from other authors. Sample preparation was carried out by R. Thomas. Remodelling was carried out by R. Thomas with assistance from D. Lunt and A. Orozco-Caballero. Data collection on the SEM was carried out by R. Thomas and D. Lunt. Data analysis and figure generation was carried out by R. Thomas and D. Lunt. Data analysis and figure generation was carried out by R. Thomas and D. Lunt using baseline scripts written by M. Atkinson. Material was provided by Westinghouse. Industrial support was provided by P. Honniball on behalf of Rolls-Royce Plc. The first draft was written by D. Lunt with comments and revision by other authors.

## Abstract

High Resolution Digital Image Correlation (HRDIC) has been established recently as a novel displacement mapping technique during mechanical loading experiments to quantify strain localisation down to the level of individual slip traces. This is achieved by the creation of a nano-scale gold pattern naturally formed during remodelling of a thin gold layer that was sputtered onto the region of interest. To date, the gold remodelling is carried out in a water vaporisation environment, which excludes the technique to be applied to materials that readily form noticeable oxide layers in such environments. The current paper describes a

recently developed gold remodelling technique using a styrene-argon environment at substantially lower temperatures than the water-vapour based technique. The material used in the present work is a zirconium alloy where we first demonstrate the problem of oxide formation during remodelling in water vapour and the benefit of the modified remodelling procedure. The error associated with the spatial drift was assessed for different interrogation window sizes followed by detailed analysis of the subsequent strain maps produced using the styrene remodelled patterns after tensile deformation to nominal applied strains of  $\sim 3.5\%$  and  $\sim 7.0\%$ . The level of detail captured demonstrate the suitability of styrene-argon-based remodelling for materials like Zr alloys with the strain maps showing clear strain patterning on both a transgranular and single grain scale with the possibility of strain across a single slip trace.

# **Keywords**

High-Resolution Digital Image Correlation (HRDIC); gold remodelling; zirconium alloy; strain localisation; plasticity; nanoscale

# Highlights

- Optimisation of speckle patterns suitable for high resolution digital image correlation in a zirconium alloy
- Evidence of distinct strain patterning at the macro and micro scale
- Analysis of strain heterogeneity in a neighbouring low and high strain band
- Paper has paved the way for future studies on strain localization in Zirconium alloys subjected to hydriding and/or irradiation damage

#### Introduction

Digital Image Correlation (DIC) is a widely used technique to measure full-field surface displacement and hence strain maps at spatial resolutions from the macro to the nano scale [174,180,185,207–216]. The spatial resolution is dependent on the speckle pattern that is applied to the surface of the sample and recently Dong and Pan [182] provided an overview of the different speckle patterns for different resolutions and the fabrication techniques used to apply them, along with an assessment of the methods with the aim of providing practical guidelines for DIC users. While DIC has long been established as a technique to determine macroscopic 2D strain fields [16,17] recent advances in High Resolution Digital Image Correlation (HRDIC) technique has opened up quantification of heterogeneous deformation from slip band formation [218]. In principle, the measurement of local shear strain enables one to assess and compare the true level of strain heterogeneity for different alloy chemistries, microstructures and the effect of microstructure inhomogeneity. Previous studies using optically based DIC have focussed on strain localisation at the microscale, reporting maximum strain concentrations ranging between 2-3.5 times the average macroscopic strain [219,220]. Di Gioacchino and Fonseca [174] developed a high spatial resolution strain mapping methodology using SEM imaging in combination with DIC that provides detailed understanding of the deformation behaviour at the sub-grain scale through quantification of the shear strain within individual slip traces, leading to a much more detailed characterisation of the strain heterogeneity. The dramatic improvement in spatial resolution demonstrated that maximum shear strain concentrations are usually 10-20 times greater than the macroscopic strain [186]. In addition, recording the shear strain associated with slip traces and combining this information with EBSD-based orientation imaging enables one now to undertake truly quantitative slip trace analysis.

The gold remodelling technique for applying a speckle pattern to the surface of a material was first developed by Luo et al. [200] on glass slides, by flowing nitrogen gas through an iodobenzene reservoir for thin gold films to form nano-sized gold islands. The technique was further developed by Di Gioacchinno and da Fonseca. [186] for DIC studies to observe the plastic deformation patterns on the surface of metals. In this case, a thin gold film deposited on flat mechanical test samples is exposed to water vapour at 300°C for 90

minutes, which results in the formation of a nanoscale speckle pattern with well-defined features that conserve their shape during plastic deformation. During exposure to heat and water vapour, the thin gold film de-wets and forms either distinct speckles or mesh-like pattern morphologies that provide high contrast compared to the substrate when imaged by Backscatter Electron Imaging (BEI) in a SEM.

However, there are a number of materials, which readily form either protective or nonprotective oxides in high temperature steam environments. Zirconium, a material used by the nuclear industry for fuel cladding due to its low neutron cross-section [5], has a particularly high affinity to oxygen and readily forms a protective oxide layer of 1-2  $\mu$ m in high temperature steam [221–223]. As a result, previous attempts to use the water vaporisation gold remodelling technique for HRDIC in a zirconium alloy (Zircaloy-4) have proved unsuccessful. The remodelling process created an oxide layer on the surface of the sample, that masked the underlying plasticity, with the subsequent strain maps demonstrating oxide cracking, Figure 4.1.



*Figure 4.1.* Maximum shear strain map for Zircaloy-4 after speckle pattern formation using gold remodelling in a water vaporization environment at (a) 4.9%, (b) 8.2% and (c) 9.5% compression.

Quantifying the level of strain localisation is important for zirconium alloys for a number of reasons. Firstly, the low temperature phase of zirconium has a hexagonal-close packed (hcp) crystal structure, and like titanium and magnesium alloys, can deform on a number of different slip systems, which makes plasticity studies particularly interesting. The ease of slip has a strong dependency on the crystallographic orientation with prismatic <a> slip reported to be the easiest slip mode in zirconium compared to basal <a> slip [55] and the more difficult to activate slip modes that contain a <c> component [16,224,225]. Secondly, the primary application of zirconium alloys (structural material for nuclear fuel assemblies) means that they are subjected to neutron irradiation, which is known to affect deformation mechanisms and lead to severe slip localisation [41,92,226,227].

The deformation of zirconium alloys has previously been studied at the micro-scale using both DIC of optical images [180] and SEM images after pattern application using the microlithography technique [185]. Héripré et al. [185] found local strain concentrations of 4 times the applied strain and high strain localisation at boundaries between grains with low and high Schmid factors for easy slip during uniaxial tension experiments on zirconium grade 702. Similar findings were reported by Padilla et al. [180] during compression testing revealing strain hot spots that were correlated with grains favourably oriented for easily activated prismatic slip. Strain patterning was visible at both length scales [180,185], with distinct low and high strain bands at  $\pm$  45° to the loading direction. It is important to note that these strain measurements were at a maximum spatial resolution of 2 µm limiting subgrain information.

In the present study, we have optimised an alternative method for remodelling a thin gold film based on the use of styrene [167] as a remodelling reagent in order to avoid oxide formation during remodelling. The suitability of the method for use for 2D strain localisation mapping during plastic deformation using HRDIC is assessed in a zirconium alloy, where previous attempts using water vapour gold remodelling have been unable to resolve fine-scale deformation.

#### **Experimental Procedure**

#### Material and mechanical loading

The gold remodelling and HRDIC-based slip localisation studies were carried out on the nuclear-grade zirconium alloy, ZIRLO<sup>™</sup> (Zr-0.9Nb-0.9Sn-0.1Fe). The recrystallised ZIRLO<sup>™</sup> sheet material was provided by Westinghouse. Tensile specimens for mechanical testing and speckle characterisation were machined from 0.7 mm thick sheet material by electric discharge machining. The tensile specimens had a flat dog bone geometry with a 26 mm gauge length and 3 mm gauge width. The surface for gold remodelling was prepared by grinding and polishing to #800 grit paper, followed by diamond polishing to 1  $\mu$ m and subsequent hand polishing for 30 minutes on an OPS cloth in a solution of 4:1 OPS to hydrogen peroxide. After polishing, a series of micro hardness indents were made on the surface of the specimen to act as fiducial markers and subsequently mapped by EBSD on a FEI Quanta 650 Field Emission Gun (FEG)-SEM equipped with an Aztec EBSD system and a Nordlys II detector. EBSD was performed at an accelerating voltage of 20 kV. An area of  $0.25 \times 0.25 \text{ mm}^2$  was analysed with a step size of 0.5  $\mu$ m to provide a sufficiently detailed grain orientation map. The data (confidence index > 0.1) were analysed using HKL Channel 5<sup>™</sup> software. Subsequently, styrene remodelling was carried out before tensile loading the specimen incrementally with strain rate of about 6.4 x 10<sup>-5</sup> s<sup>-1</sup> using a Kammrath-Weiss 5 kN Tension-Compression microtester. As the working distance for optimal imaging conditions in the SEM was less than 6mm and the microtester requires a larger working distance when installed inside the microscope, the experiments were carried out ex-situ. Hence, after each deformation step the sample was removed from the microtester and mounted in the SEM for image acquisition.

#### Application of speckle pattern

A thin gold layer of 25-40 nm was deposited on to the surface of the sample using an Edwards S150B sputter coater at a deposition rate of 5-8 nm/min. The parameters for the sample remodelled in water vapour (Figure 4.1) were 200°C for 3 hours using the method detailed in [174]. The alternative methodology suitable for temperature sensitive/readily oxide forming materials was developed using styrene as an alternative solvent to water

vapour and has been proven to be successful for HRDIC on a magnesium alloy [167]. This method requires the remodelling chamber to be isolated to remove oxygen from the process. Once the gold layer has been deposited onto the polished sample surfaces, the samples are placed into the chamber shown schematically in Figure 4.2. The remodelling process begins by initially flowing argon gas through a styrene reservoir, in turn creating a mixture of argon and styrene vapour. A hot plate, which has a flat surface to provide a homogeneous temperature distribution across the sample, is positioned in the centre of the remodelling chamber. Its temperature can be monitored and adjusted using an external control unit. The Ar-Styrene flow is passed directly over the sample surface and subsequently remodels the gold layer into fine speckles. The chosen styrene remodelling temperature was 200°C and individual samples were remodelled for 20 minutes, 12 hours, 2 days, 3 days, 4 days and 6 days, respectively.



Figure 4.2. Schematic of the experimental apparatus for styrene assisted remodelling.

#### Imaging

Gold remodelling in a styrene environment has previously been shown to generate speckle patterns with a finer size distribution compared to the patterns generated after remodelling in a water vaporisation environment [167]. Therefore, a higher resolution microscope and different imaging conditions were utilised to obtain the desired level of details, brightness and contrast in the images. The image size and magnification were chosen such that speckles were defined by at least 4 pixels in the recorded images [174]. The images were acquired using an FEI Magellan FEG-SEM in immersion and back-scattered electron imaging mode at an accelerating voltage of 1 kV and a current of 0.8 nA, with a 2 kV stage bias. The working distance was approximately 3 mm, at magnifications giving horizontal field widths of 20  $\mu$ m. Each image took 30 seconds to record and all images were acquired at a resolution of 2048 x 1768 pixels<sup>2</sup> in a scan mode with a 10  $\mu$ s dwell time. A matrix of 10 x 10 images was recorded using FEI MAPS software with a 40% overlap and the images were focussed using a 3-point focus correlation function. This provided a total horizontal field width of 121  $\mu$ m for HRDIC analysis.

Drift correction was not applied, as the shifts in the beam position are only fractions of a pixel and calculating the systematic error associated with the spatial drift factors these in. The images were also collected at a small working distance, as this helps to minimise the spatial drift [169,174,228]. The systematic error was calculated by comparing two images from the same region before deformation and then using decreasing interrogation window sizes to find the optimal interrogation window to perform the strain analysis [174].

## **Digital Image Correlation**

Digital Image Correlation (DIC) is principally the tracking of features from the same region before and after deformation, which is used to calculate the relative displacement of these features throughout the deformation [166,191,229]. The displacements are then differentiated to compute the desired strain field. The DIC strain maps calculated in this study are presented in terms of effective shear strain because this term takes into account all the components of the in-plane strain tensor [174,186]. The effective shear strain ( $\varepsilon_{max}$ ) was calculated using equation 16, where  $\varepsilon_{xx}$  is the strain in the loading direction,  $\varepsilon_{yy}$  is the in-plane strain normal to the loading direction and  $\varepsilon_{xy}$  is the in-plane shear strain. Calculating the average  $\varepsilon_{xx}$  across all images approximated the applied strain for the interrogated area.

$$\varepsilon_{\max} = \sqrt{\left(\frac{\varepsilon_{xx} - \varepsilon_{yy}}{2}\right)^2 + \varepsilon_{xy}^2},$$
(16)

The full array of images at each deformation step were stitched together before processing and then correlated with the stitched image acquired before deformation, generating a single large area strain map. The HRDIC analysis was performed using the commercially available software DaVis. Initially the images were shift and rotation corrected to align the central features for each deformation step. The local displacement was then calculated by applying a standard FFT cross correlation relative to the image prior to deformation with a final interrogation window size of 12 x 12 pixels<sup>2</sup>.

#### **Theoretical Slip Trace Angles**

Theoretical slip trace angles were determined based on the grain orientation mapping, acquired from the HRDIC region using EBSD, by calculating the theoretical slip trace angles for the required slip system using a crystal mathematical tool developed at The University of Sheffield. A Matlab script first extracts the Euler angles for each grain and calculates an average grain orientation, which is then used for determining the theoretical slip trace angles for determining the theoretical slip trace angles for grains with a Schmid factor greater than 0.35 for prismatic slip. This procedure for determining the theoretical slip trace angles for a single grain is described in more detail in [72,230]. The orientations of the experimental slip traces were determined using a Radon transform of the HRDIC strain maps thresholded to include all slip traces with a maximum shear strain greater than 10%. In this study the theoretically predicted slip trace angles are not directly correlated with the measured angles from HRDIC due to difficulty overlaying the strain map onto the grain orientation maps. The comparison between the experimental and theoretical slip trace angle is based on the strong texture of the material promoting prismatic <a> slip.

## Results

#### **Material Characterisation**

Figure 4.3 shows the orientation map from the general HRDIC region and the corresponding pole figures. The material has an equiaxed microstructure with an average grain size of ~ 5  $\mu$ m and the grains are predominantly red/orange, Figure 4.3a. Based on the average grain size, the number of grains in the HRDIC is calculated to be ~ 350 grains. The respective pole figures, Figure 4.3b, show that the material has a split basal texture with a maximum texture intensity of ~ 5 times random The material was loaded along the rolling direction, which gives a strong preference for prismatic <a> slip.



**Figure 4.3.** (a) IPF ND map of ZIRLO<sup>TM</sup> and (b) the corresponding EBSD generated (0001), {1120} and {1010} pole figures. For interpretation of the references to the colour in this figure legend the reader is referred to the web version of this article.

## Effect of remodelling time on pattern morphology

First, the speckle pattern morphology produced after different styrene remodelling times was studied to optimise the patterns. The optimal speckle pattern for DIC would have a uniform speckle size distribution [183], as speckles that are too small may be difficult to resolve and large speckles can act as featureless areas if sufficient grey scale contrast cannot be achieved. The features should be easily resolved by the respective imaging system and provide a sharp contrast relative to the underlying substrate. Figure 4.4 shows BSE images of the gold speckle patterns produced after 20 minutes, ½ day, 2 days, 3 days, 4 days and 6 days exposure to styrene vapour. Close examination of the speckle pattern development after 20 minutes in Figure 4.4a shows very fine interconnected speckle pattern morphology with almost no spacing between individual speckles. After ½ day exposure, Figure 4.4b, the speckle pattern displays a bimodal distribution. It should be noted that it was also difficult to obtain sufficient contrast between the substrate and the speckles after short remodelling times, which suggests that the gold film has not fully remodelled at this stage. There are two distinct regions, one that still has very fine interconnected gold domains and another that has developed coarser regions that remain interconnected. Figure 4.4c shows that after 2 days remodelling the interconnected gold domains have developed into individual gold speckles, which have a distance between the speckles that is equal to the size of the speckles. From this point on, the rate of change of the speckle pattern morphology reduces and this is shown in Figure 4.4d, where after 3 days there is little change in the speckle pattern. After 4 days (Figure 4.4e) the speckles are larger and more interconnected. As surface finish has been shown to significantly affect the developed speckle pattern, this is likely to be a result of using separate samples for each remodelling stage, [174]. Figure 4.4f shows the speckle pattern after 6 days exposure to styrene vapour and the speckles are not significantly different to those after 2 days remodelling, but are slightly more circular.



**Figure 4.4.** Backscattered electron images of the gold speckle patterns produced by styrene remodelling on Zirlo<sup>TM</sup> at 200°C with a 40 nm gold film thickness after (a) 20 minutes, (b)  $\frac{1}{2}$  day, (c) 2 days, (d) 3 days, (e) 4 days and (f) 6 days.

The size distribution and area fraction of the gold speckles after different remodelling times was determined using the particle analysis function in the open source software ImageJ [231] and are shown in Figure 4.5. It should be noted that for the speckle size distributions the images were individually thresholded to remove the overlapping regions between single speckles. From this figure, it was observed that both the area fraction and size

distributions appeared to plateau after 4 days exposure to styrene vapour, as the area fraction of the speckles reduces from approximately 50% to less than 40% and the speckle size increases from 10nm to greater than 25nm. Subsequently, 4 days exposure was selected as the optimal remodelling time after exposure to styrene. The size distribution of the speckles after 4 days remodelling, Figure 4.6, indicates a mean diameter of about 15-20 nm, which is significantly smaller than those observed previously after remodelling in water vapour [186]. These smaller speckles required higher magnification imaging but enable improved spatial resolution of the HRDIC-based strain measurements. The shape of the distribution also indicates a large range in the diameter of the speckles likely to be due to the interconnecting regions and small speckles.



*Figure 4.5.* Average speckle diameter and area fraction of gold speckles after different remodelling times.



Figure 4.6. Speckle size distribution after 4 days styrene remodelling at 200°C.

The systematic error was assessed, for the optimum remodelling conditions, by acquiring two sets of  $3 \times 1$  image matrices sequentially from the same region at the optimal magnification used for the HRDIC strain mapping and performing cross-correlation of the pair (3 x 1 stitch) of images. Figure 4.7 shows area profiles of the average maximum shear strain associated with the systematic error for interrogation window sizes ranging from 8 x 8 pixels<sup>2</sup> to 16 x 16 pixels<sup>2</sup>. It can be observed that the systematic error decreases exponentially with increasing interrogation window size. The average maximum shear strain value are 0.55%, 0.31% and 0.23% for 8 x 8 pixels<sup>2</sup>, 12 x 12 pixels<sup>2</sup> and 16 x 16 pixels<sup>2</sup>, respectively. Comparing to previous calculations of the systematic error for patterns remodelled in water vapour and with different imaging conditions [172], there appears to be a marginal increase in the uncertainty in average shear strain. However, the similarity indicates that the patterns produced are suitable for HRDIC deformation studies. Errors associated with distortion can be significant in SEM based measurements [169,174,212,228,232]. However, in this work, the high quality electron optics used and the favourable working conditions (high magnification, small working distance, low dwell time, etc) all help minimize these errors. Although they were not fully characterised, the strain in the images used to calculate the "error strain" in Figure 4.7 show no clear spatial correlation, implying that the errors are not just small but also random and therefore will not affect the measurement in a significant way. It is also worth noting that, because of the very high spatial resolution of the strain measurements  $(117 \times 117 \text{ nm}^2 \text{ for a } 12 \times 12 \text{ pixels}^2)$ 

interrogation window size), the local strain values are very high. Because slip is very localized, the improved spatial resolution improves the signal to noise ratio over measurements made at lower spatial resolutions. Furthermore, the images were stitched together before processing by a linear blend function using ImageJ and due to the density and strong contrast of the speckle patterns typically give a correlation confidence of > 0.9. If there had been significant distortion associated with the images, the image blending operations would have introduced significant artefacts in the stitched regions of the images, which do appear as the strain maps in Figure 4.8 show. This is also shown from the error associated with the stitched boundaries in Figure 4.7, which show an increase in strain of around 1.5-2 times the typical value but this error is still well below 1%.




### **Strain Mapping**

Based on the analysis shown in Figure 4.7, an interrogation window size of  $12 \times 12$  pixels<sup>2</sup> was chosen to provide the optimal balance between spatial resolution and data reliability. This equates to an interrogation window size of  $117 \times 117$  nm<sup>2</sup>. Figure 4.8 shows maps of maximum shear strain after tensile loading the sample to ~ 3.5% and ~ 7% strain in the loading direction. Clearly, the strain patterns here are very different to the ones presented in Figure 4.1, which were affected by cracking of the oxide formed during gold remodelling. After 3.5% tension, Figure 4.8a shows that there are intense, relatively straight bands of high and low shear strain at 45° and 135° to the loading direction and these appear to have developed in a strain pattern across the sample. Within the high strain bands, it can be observed that there are single slip traces at 90° to the macro strain bands. Figure 4.8b shows a further progression in the development of slip band formation and shear strain intensification within shear traces with maximum local shear strains of over 30% at the boundaries between the high and low strain regions.



**Figure 4.8.** Maximum shear strain maps for  $ZIRLO^{TM}$  after (a) 3.5% and (b) 6.8% tension.

#### **Trace Analysis**

The observed deformation behaviour from the strain maps was compared to the theoretical slip activity of the underlying microstructure, Figure 4.9, by determining the theoretical slip trace angles using grain orientation data in the DIC regions. Slip trace analysis could not be performed in the traditional way (on a grain to grain basis), as it was not possible to accurately overlay the grain boundaries from EBSD onto the HRDIC strain map due to the small grain size and lack of distinguishable features. Therefore, from the EBSD orientation data, grains included in the theoretical analysis were chosen to be those well aligned for prismatic <a> slip, i.e. grains with a global Schmid factor greater than 0.35 for this slip mode. This criterion was used as the strong texture of the material in conjunction with the loading direction promotes prismatic <a> slip in the present case, which is also known to have the lowest critical resolved shear stress [51]. It should be noted that over 95% of the 126 grains analysed passed this criterion further emphasising the strong likelihood of prismatic <a> slip being the dominant slip mode. The experimental slip trace angles were calculated using a Radon transform of the HRDIC strain maps thresholded to only include maximum shear strains greater than 10%. Figure 4.9 shows that there is a strong agreement between the HRDIC and slip trace analysis angles with distinct peaks at about 35-50° and 130-140° to the loading direction. There are notable differences between the shapes of the two curves, but this can be attributed to the experimental slip trace angle taking into account every slip trace in each grain above the threshold and the theoretical slip trace angle only considering one slip trace angle per grain.



**Figure 4.9.** Comparison of theoretical predicted slip trace angles with measured slip trace angle from HRDIC strain maps.

## Discussion

### **Pattern Optimisation**

An alternative method for remodelling a thin gold film, based on the use of styrene as a remodelling reagent, for corrosion susceptible materials has been utilised to produce a speckle pattern suitable for HRDIC on a zirconium alloy. The equipment design allows a mixture of Ar-Styrene to flow over the sample (without oxygen) and enables the thin gold film to dewet from the surface and subsequently remodel. This method has been developed based on previous studies using water vapour [174] and iodobenzene [200] and has proved similarly successful in producing nano-size speckle patterns on the surface of a sample when remodelling at a temperature of 200°C. The remodelling temperature has been reduced compared to remodelling in a water vaporisation environment, as this opens up the possibility to apply this methodology to materials that are sensitive to temperatures greater than 200°C and water-based steam. This is particularly the case for studying zirconium alloys, as it readily forms a protective oxide of a few microns when exposed to water vapour. In addition, studying strain localisation in irradiated material requires remodelling temperatures that do not anneal out the irradiation-induced defect structure. Therefore, it is essential to minimise the remodelling temperature to ensure that the

properties of the underlying material are not significantly changed. The optimisation of the remodelling parameters, when exposed to styrene, showed the development of small and well defined speckles with increasing remodelling time, similar to previous observations by Luo et al. [200], when remodelling using iodobenzene on glass slides. The speckle diameter increased overtime from about 10 nm after 20 minutes remodelling up to about 25 nm after 6 days. This was in combination with a reduction of the area fraction occupied by the gold speckles from over 50% after 20 minutes to below 40% after 6 days. Another distinct feature of the morphological evolution over time was the increased circularity of the speckles. This development in the speckle pattern is likely to be due to the prolonged thermal dewetting with increasing remodelling time leading to the coalescence of adjacent speckles, reduction in speckle area fraction and evolution to round speckle shapes to minimise the total surface energy [233]. The smaller speckle size for the samples remodelled in styrene is thought to be a result of the lower remodelling temperature, as previous work [233] on the speckle evolution with temperature have shown the development from small mesh features to large circular speckles with increasing temperature. Previous work suggests that the remodelling vapour does not have a significant effect on the difference in speckle size, as comparing the speckle patterns developed in water and iodobenzene vapour at the same temperature showed similar speckle size distributions [200].

HR-DIC analysis using the optimised speckle pattern after 4 days remodelling indicated a marginal increase in the systematic error compared to previous HRDIC studies using water vapour as the remodelling reagent. This can be attributed to the smaller speckle size after remodelling in styrene reducing the backscattered electron signal intensity. However, this is insignificant as the peak strains recorded using HR-DIC are typically of the order of 10 times the applied strain [174]. One implication of producing a pattern with a finer speckle size in the styrene remodelled sample is that a microscope with higher spatial resolution is required to provide sufficient detail and contrast from the smaller speckles. However, through the utilisation of automated stage mapping (FEI MAPS software) a series of high resolution images were captured over a statistically relevant area (about 100 x 120  $\mu$ m<sup>2</sup> equating to 350-400 grains) thus providing large strain maps whilst maintaining a high spatial resolution.

#### **Strain Mapping**

Previous HR-DIC studies [167,172,174,186,234] showed that when deforming samples with a gold speckle pattern applied using the gold remodelling process, the gold speckles adhere to the surface and are easily distinguishable after plastic deformation. This is crucial in providing high accuracy strain measurements at sub-micron resolution. In the current work, significant strain patterning on the macro and micro-scale was observed, with large low and high shear strain bands at 45° to the loading direction. This periodic variation of transgranular shear bands at about 45° to the loading direction has also previously been observed in stainless steel [174] and zirconium alloys [195]. The deformation within the transgranular shear bands is also highly heterogeneous with many planar slip traces per grain that are in many cases perpendicular to the direction of the bands. Additional grain orientation mapping using EBSD also confirmed that the observed slip traces are likely to coincide with possible prismatic slip systems. Determination of theoretical slip trace angles and experimental slip trace angles from HRDIC strain maps showed that grains favourably oriented for prismatic <a> slip displayed similar slip trace angle distributions with a high density of slip traces aligned at 35-50° and 130-140° to the loading direction. This was expected, as the majority of grains were favourably oriented for this slip system. The high resolution of the strain measurements, from using styrene remodelling as the speckle pattern application, allows single slip traces to be resolved within deformed grains. This provides the possibility of slip system characterisation on a grain by grain basis using the slip trace analysis technique used in previous studies on magnesium [167] and titanium [172] alloys.

By utilising the styrene vapour assisted gold remodelling technique in combination with SEM imaging, it is now possible to gain an understanding of the strain localisation that occurs across a material by analysing and comparing the strain distributions in different regions of a sample. The significant strain patterning that has been observed in this work has been analysed further in Figure 4.10, by investigating the difference in strain localisation between a neighbouring low (R1) and high (R2) strain region. Figure 4.10a shows that the key difference in the strain localisation, at 3.5% applied strain, was the presence of several cold spots in R1 compared to a higher slip trace density in R2, as the

bulk strain in the matrix appears to be similar. With increasing applied strain, Figure 4.10b, there appears to be further slip accumulation in R2 with the development of new slip traces and an increase in the strain in the slip traces that were present previously. This is also evident for R1, but with lower strain intensities in the slip traces. Figure 4.10c quantifies the strain localisation using normalised frequency distributions, at 3.5% applied strain, and shows a marked difference in the strain heterogeneity between the two regions. The maximum strains observed in R2 are a factor of 2 higher than in R1. Figure 4.10d, at 6.8% applied strain, indicating that the strain accumulation in the two regions appears to have increased proportionally with increasing macroscopic strain.



**Figure 4.10.** Maximum shear strain maps of  $ZIRLO^{TM}$  after gold remodelling in a styrene environment at (a) 3.5% and (b) 6.8% tension with R1 and R2 indicated in orange and red, respectively, and the normalised frequency distributions of the maximum shear strain for regions 1 and 2 at (c) 3.5% and (d) 6.8% local strain.

Uniformly spaced and regular neighbouring low and high strain bands appears to be a distinct feature of the strain localisation that develops in zirconium alloys, as it has also been observed in zirconium grade 702 [180,185], M5 alloy [195] and Zircaloy-4 [195]. These studies provided detailed strain information at the grain-to-grain level giving local strain concentrations with a maximum of 4 times the applied strain in the high strain bands. Similarly, Padilla et al. [180] also found a direct correlation between high strain hot spots and grains favourably oriented for prismatic slip. However, due to the lack of detailed sub grain information these studies do not capture many of the features that are important for understanding the failure mechanisms. The current work has been able to demonstrate that there are in fact significant strain concentrations up to 10 times the applied macroscopic strain across single grains, e.g. high strain slip traces with little deformation between the traces and also intense strain localisation near grain boundaries. It is also apparent that even within a high transgranular strain band there is significant strain heterogeneity with single grains that still remain undeformed. Hence, the Ar-styrene remodelling methodology has enabled now detailed plasticity studies of zirconium alloys that will be applied to quantify the effect of typical degradation modes such as irradiation damage and hydride formation on strain localisation and investigate potential changes in slip modes.

## Conclusions

Existing experimental settings for the gold remodelling technique were adapted by using styrene as the remodelling vapour, successfully enabling high-resolution deformation mapping in zirconium. The effect of time on the remodelling process was studied by exposing the samples to styrene from 20 minutes to 6 days. The key stages in the pattern development were from very fine interconnected speckles at short remodelling times to the development of well-defined individual speckles at longer remodelling times. The optimum remodelling conditions were a 40nm initial film thickness remodelled at 200°C for about 4 days, as the pattern development appeared to plateau around this time period. The reduced speckle size increased the systematic error of the strain measurements when resolving the patterns at the same interrogation window size, as previous studies using the water vaporisation technique for applying the speckle pattern.

The strain maps for ZIRLO<sup>™</sup> demonstrated significant strain patterning on a macro to sub micron scale with the possibility of measuring the strain accumulation across macro strain bands to single slip traces. There was no evidence of oxide cracking from the strain maps. The evolution of local strain was studied at 3.5% and 6.8% macroscopic strain and maximum shear strain values of 6 times the applied strain were observed across single slip traces.

In conclusion, it has been shown that it is possible to study the local deformation behaviour on the sub-micron scale in zirconium alloys. The smaller speckle size generated after the alternative remodelling technique increases the spatial resolution of the strain measurements, as higher magnification images are required. This technique, used in combination with recent developments in automatic image acquisition, means that it is now possible to measure strain in oxygen-sensitive materials such as zirconium alloys at the nanoscale over large areas, allowing sub-grain scale deformation to be investigated over a statistically relevant number of grains. For zirconium alloys this now opens up the possibility to study slip system activity and slip localization caused by irradiation and hydriding, two important degradation modes for nuclear fuel cladding that affect its structural integrity.

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# 5. Characterisation of irradiation enhanced strain localisation in a zirconium alloy

<u>*R.*</u> Thomas<sup>1</sup>, D. Lunt<sup>1</sup>, M.D. Atkinson<sup>1</sup>, J. Quinta da Fonseca<sup>1</sup>, M. Preuss<sup>1</sup>, F. Barton<sup>2</sup>, J O'Hanlon<sup>2</sup>, P. Frankel<sup>1</sup>

<sup>1</sup> School of Materials, University of Manchester, Manchester, UK.
 <sup>2</sup> Rolls-Royce Plc, Derby, UK.

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# **Contribution statement**

The experiment and proton irradiation campaign were designed by R. Thomas with input from supervisors, P. Frankel and M. Preuss. Sample preparation was carried out by R. Thomas. Data collection on the SEM was primarily carried out by R. Thomas with assistance from D. Lunt. Data analysis and figure generation was performed by R. Thomas using baseline scripts written by M. Atkinson. Material and industrial support was provided by F. Barton and J. O'Hanlon on behalf of Rolls-Royce Plc. The first draft was written by R. Thomas with comments and revision by other authors.

# Abstract

High resolution digital image correlation (HRDIC) has been used to quantify the effect of proton irradiation on strain localisation in Zircaloy-4. Confinement of slip to dislocation channels in irradiated material lead to intense, planar slip bands with high effective shear strain values within channels. More diffuse, homogenous slip was observed in non-irradiated material, with the highest strains measured near grain boundaries. By comparing experimental slip trace angles from HR-DIC with theoretical slip trace angles determined using grain orientations from electron backscatter diffraction (EBSD), the active slip plane

was determined. Understanding the localised deformation of irradiated materials relative to their microstructure is essential for valid predictions of the structural integrity, and therefore design life, of components in nuclear applications.

# Keywords

Plasticity, Slip, Electron Backscatter Diffraction (EBSD), Irradiation embrittlement, High Resolution Digital Image Correlation (HRDIC)

# **Graphical Abstract**



### Manuscript

Zirconium alloys are widely used in the nuclear industry, as structural components for fuel assemblies inside nuclear cores, due to their low neutron absorption cross section and good mechanical strength and corrosion resistance at reactor operating temperatures [5]. In service, these components are exposed to neutrons produced by the fission process. This significantly impacts on the macroscopic mechanical properties by increasing the strength but decreasing the ductility of the material, with increasing fluence [11,12]. Transmission Electron Microscopy (TEM) investigations have suggested that this is a result of <a> type prismatic loops forming, which act as obstacles to dislocation glide during plastic deformation [41,87]. When sufficient stress is applied, the dislocations can annihilate or drag loops, causing thin channels that are free of defects [89,92]. Subsequently, these channels act as further dislocation glide paths leading to regions of intense, localised plastic deformation [24,41]. Although dislocation channels have been observed in TEM investigations and the effect of irradiation damage on mechanical property changes has been quantified, the link between the channelling mechanism and microscopic deformation behaviour has rarely been studied.

In-reactor microstructural damage is due to neutron irradiation, however, producing and handling neutron irradiated samples is both a time consuming and expensive process [97]. Proton irradiation is increasingly used as a surrogate for neutron irradiation to investigate the effect of irradiation damage in structural materials such as steels [235–237] and zirconium alloys [34,80,99,100]. Since only a thin region at the surface is irradiated, investigation of deformation behaviour at the surface using high resolution digital image correlation (HRDIC) [166,167,172,174,216] is appropriate. Recent developments in surface patterning techniques, in combination with high-resolution imaging and automated image mapping in a SEM, have opened up the possibility of investigating deformation patterns well below the sub-grain scale level over a statistically relevant number of grains [238]. In the present work, HRDIC has enabled quantification of the increase in strain localisation when a Zr-based alloy was irradiated. The change in deformation behaviour is discussed in the context of dislocation channelling, underlying microstructure and slip system activity.

This provides a basis on which models of local strain in irradiated materials can be validated.

The material investigated in this study is recrystallised Zircaloy-4, nominally Zr-1.5Sn-0.2Fe-0.1Cr (wt%) [239], supplied by Rolls-Royce Plc. The average grain size of the material was measured using electron back-scatter diffraction (EBSD) to be 9  $\mu$ m. Texture analysis shows a 'split-basal' texture, where basal poles preferentially orient in ND with a spread of ± 28° in TD. The RD-TD plane of the sample used in this study was ground, polished with diamond paste and finally hand polished with 0.06  $\mu$ m colloidal silica solution (diluted with 20% hydrogen peroxide) for 30 minutes. The central 1.3 mm of the specimen's polished surface was subjected to irradiation at the Dalton Cumbrian Facility's ion accelerator [198], using 2 MeV protons at 357 ± 2 °C and a current of 12.8  $\mu$ A cm<sup>-2</sup>. Proton irradiation produces a variable profile of damage with depth [97], but calculations suggest a fairly uniform damage of between 0.09 and 0.13 dpa in the outermost 15  $\mu$ m. The baseline hardness of the material was 180 ± 6 HV and hardness in the irradiated region was 219 ± 5 HV, which corresponds to a hardness increase of 22%.

For strain analysis using HRDIC, a gold speckle pattern was produced on the sample surface using the styrene remodelling technique [238], at a temperature of 150°C for 3 days. Exsitu uniaxial tensile deformation was carried out along RD, at room temperature, at an initial strain rate of  $1.6 \times 10^{-4} s^{-1}$ . Images for HRDIC analysis were acquired before and after deformation using a FEI Magellan Field Emission Gun (FEG)-SEM, in Back-Scattered Electron (BSE) imaging mode at an accelerating voltage of 5 kV in immersion mode with a 2 kV stage bias, at a working distance of 3.4 mm. Images were acquired with a horizontal field width (HFW) of 10 µm, at a resolution of 2048 x 1768 pixel<sup>2</sup>, and a dwell time of 10 µs. An array of 16 x 16 images<sup>2</sup> equating to 120 x 100 µm<sup>2</sup> containing over 100 grains was captured using FEI MAPS software. The images for each deformation step were stitched together before processing using the Grid/Collection stitching function in ImageJ [205] with a linear blend applied. HRDIC analysis was performed using the commercially available LaVision Davis 8.1.5 software, using a fast Fourier transform (FFT) correlation method, with a final interrogation window size of 16 x 16 pixels<sup>2</sup>, corresponding to 78 x 78 nm<sup>2</sup>. The data were analysed using in-house Python routines and the NumPy numerical library [240]. The Matplotlib library [241] was used for visualisation. By differentiation of the in-plane displacement field, the components of the strain tensor can be determined. In order to better visualise the data, effective shear strain is used [167,174] which interprets all strains as shear strains and is therefore a good scalar representation of local deformation at submicron scale since most room temperature deformation occurs by shearing of the lattice [174]. By correlating two successive undeformed images, the average effective shear strain error was measured to be 0.17%. Grain orientation maps of the HRDIC regions were obtained after the last deformation step with a step size of 0.2  $\mu$ m, to enable a detailed correlation between the grain orientation and strain data. Lattice rotations are plotted as the in-plane rotation component (to allow comparison with DIC) with respect to the mean deformed grain orientation.

The active slip system in a grain was determined using traditional slip trace analysis [230], where the experimentally measured slip trace angles from HRDIC were compared with the theoretical slip trace angles for all slip planes under consideration (basal (1), prismatic (3) and first-order pyramidal (6)), calculated using grain orientation from EBSD. It should be noted that using this technique it is not possible to differentiate between pyramidal <a> and pyramidal 1st order <c+a> as they provide the same slip trace angle with respect to the plane and they are therefore grouped together as pyramidal slip. An acceptance angle of  $\pm^{\circ}$ 5 degrees was chosen and if more than one slip system lies within this criterion (~40-50% of total cases) the grain is disregarded from further slip system analysis.

From the HRDIC data, an average strain in the loading direction of 2.59% was calculated in the non-irradiated region compared to 2.04% in the irradiated region, consistent with the 22% hardness increase measured using microhardness indents. The maps obtained by HRDIC, for the two different regions, are presented in Figure 5.1a and b. The grain boundaries, with a critical misorientation of 4°, have been overlaid (in white) by applying an affine transformation to the EBSD data such that it aligns with the strain map. Although formally a projective transform is required to correct for trapezoidal or rhomboidal tilt distortions, an affine transform was sufficient to register the datasets in this case. Both regions exhibit local heterogeneity, but with very distinct differences in terms of both strain intensity and location.

Focussing on the non-irradiated region (Figure 5.1a), the strain localisation appears diffuse with closely spaced and indistinct individual slip bands. In comparison, the strain localisation in the irradiated region (Figure 5.1b) is significantly different with distinct slip traces that are highly planar and have higher effective shear strains. The large difference in strain localisation between the slip traces and the matrix can be clearly observed with little strain observed in the regions between the slip traces. In comparison, there is little difference in strain between the slip bands and the matrix in the non-irradiated map, with the value fluctuating about the mean as opposed to reducing to almost zero between slip traces in the irradiated region. The regions of highest strain in the non-irradiated material, are typically located on or near grain boundaries, whereas in the irradiated material the highest strains are largely contained in dislocation channels near grain centres.

The combination of the texture relative to the loading direction and the low critical resolved shear stress for prismatic slip in zirconium, means prismatic slip is the most likely deformation mode [50]. Figure 5.1c and d show maps of maximum Schmid factor for prismatic slip based on average grain orientation, with the red points overlaid to indicate regions where the effective shear strain is greater than the 95th percentile. Where a unique solution for the active slip plane in a grain was determined from slip trace analysis, it is shown in Figure 5.1c and d. The results are also summarised in Table 5.1. In 94% of cases in the non-irradiated region, the active slip system was determined to be prismatic, while the rest were pyramidal. In the irradiated region, 91% of grains exhibit prismatic slip with the remainder being pyramidal. Similar observations were made in a TEM study by Onimus et al. [41] who observed prismatic channels in 14 of 18 grains (78%) and pyramidal in the remainder. It should be noted that the alloy studied was Zr-1wt%Nb, neutron irradiation was performed and the testing temperature was 350 °C as opposed to room temperature in this study which may account for the small difference in slip system activity.

		Pr	Ру	Ambiguous
This study	Non-irradiated	31	2	17
	0.1 dpa proton irradiated	31	3	35
Onimus et al. [5]	$12 \times 10^{25}$ n m <sup>-2</sup> neutron irradiated	14	4	2

**Table 5.1.** Slip system activity determined by slip trace analysis for non-irradiated and irradiated regions in this study, compared with literature.

Grain boundary shear, defined as discrete strain following the contour of a grain boundary is highlighted in blue in Figure 5.1 c-d). In some cases that grain boundaries are misplaced by a few pixels due to the simple affine transformation applied to align the EBSD data to the DIC. Instances of grain boundary shear are more common in the non-irradiated region. Grain boundary shear has also been observed by Padilla et al. [180] and Héripré et al. [185] in non-irradiated zirconium between grains which are favourably oriented for different slip modes. In this study, it appears to occur in grain boundaries irrespective of the difference in Schmid factor for prismatic slip.

In grains with two or more dislocation channels with effective shear strains greater than 5%, the average spacing between channels was measured to be  $1.60 \pm 0.85 \,\mu$ m. This agrees with TEM studies in neutron irradiated material [41], where the average grain size was 8  $\mu$ m and the average number of channels per grain was 5, giving a spacing of ~1.5  $\mu$ m. The average width of a channel was measured to be  $0.32 \pm 0.16 \,\mu$ m. This width is around 4 times larger than measured previously by TEM in both neutron [41] and 2 dpa proton irradiated [96] Zircaloy-4. This is because DIC measures the accumulated strain during deformation, whereas TEM only shows the clear band where loops have been swept. The latter is likely to be smaller since the strain field can extend beyond the channel. It is also possible that the lower macroscopic strains investigated in the previous TEM studies contributed to the thinner channels.



**Figure 5.1. Strain distribution maps.** Effective shear strain maps of the a) non-irradiated and b) irradiated regions. Below, skeleton maps showing average Schmid factor for prismatic slip, overlaid with 95th percentile of effective shear strain in red and grain boundary shear in blue for the c) non-irradiated and d) irradiated regions. Where a unique slip plane was identified using slip trace analysis, this system is noted. Dashed boxes indicate regions investigated in more detail later.

The clear difference in strain heterogeneity observed can be further supported by quantitative analysis of the strain data for the two regions in terms of frequency distributions of effective shear strain (Figure 5.2). The axes limits were chosen to only show bins with more than 10 points such that pixels associated with noise are not displayed. The effective shear strain values have been normalised by dividing them by the average effective shear strain for each region, due to the difference in average strain for each. As the tails (highest strain values) of the frequency distributions are the most important in terms of mechanical performance (crack initiation) the data has been plotted on a log-log scale [172,242]. These tails are present above about 4 multiples of average effective shear

strain but are more pronounced in the irradiated data. This is attributed to the high plastic strain localisation exhibited by the more intense slip in dislocation channels. The frequency distribution for the non-irradiated region is narrower, corresponding to a more homogeneous distribution. As a result, the frequency of points near the mean effective shear strain is higher in the non-irradiated region. For low strains (multiples of average effective shear strain less than 0.7), the frequency is higher for the irradiated data. This is due to the areas outside the dislocation channels accumulating very little deformation as the channels act as easy paths for slip.

Another way of quantifying the degree of strain heterogeneity is by calculating the ratio between the 99.99<sup>th</sup> percentile and the 0.01<sup>th</sup> percentile value of effective shear strain. This ratio is 6.9 times larger for the irradiated region compared to the non-irradiated region. These values are also indicated on the histogram in Figure 5.2. It should be noted that the 99.99<sup>th</sup> and 0.01<sup>th</sup> percentile are used instead of the maximum and minimum value to exclude any effect of noise from single pixels of high or low strain.



**Figure 5.2. Effective shear strain frequency.** Histogram of effective shear strain for non-irradiated (green) and irradiated (red) regions, normalised against the average effective shear strain for each region, plotted on a log-log scale. Positions of  $0.01^{\text{th}}$  and  $99.9^{\text{th}}$  percentiles are indicated by  $P_{0.01}$  and  $P_{99.99}$ .

By isolating particular grain combinations in the map, a more detailed investigation of the relationship between shear strain and lattice rotation can be carried out. In the nonirradiated region, the in-plane rotation map from EBSD show smooth gradients within most grains, as highlighted by the grain shown in Figure 5.3 (taken from the dotted box in Figure 5.1c). The effective shear strain map (Figure 5.3b) shows that two different prismatic slip planes are active in the grain. The system with highest strain is at 114° to the horizontal and EBSD data shows a counter-clockwise rotation, relative to the mean orientation. The majority of high strain points are located within this region (Figure 5.3a). The slip band spacing was measured to be 100-250 nm, which is significantly lower than for the irradiated region. In-plane rotation reaches a maximum of 3.5° and in this grain correlates to a region where the most strain is due to slip bands, but this is not the case in all grains. Below the region of primary slip, another prismatic slip system is active at 70° to the horizontal and is associated with a clockwise rotation. These observations are similar to the formation of deformation domains in stainless steel [186], but have not been observed before in zirconium alloys. In the lower domain, the slip bands are harder to distinguish and the inplane rotation reaches a maximum of 2.5°, even though the effective shear strains in this region are half that of the other domain.



**Figure 5.3.** Deformation domains in a non-irradiated grain. a) Skeleton map showing average Schmid factor for prismatic slip, overlaid with 90th percentile of effective shear strain. Grain orientation and theoretical slip plane angles with Schmid factor are inset to the left. b) Effective shear strain map. c) In-plane lattice rotation relative to the mean grain orientation. Region taken from dotted box in Figure 5.1c.

The confinement of plastic deformation in irradiated material to dislocation channels causes large strain localisations within grains, leading to high stresses at grain boundaries. In the irradiated region slip bands are observed to continue through grain boundaries more commonly than in the non-irradiated region. It has been suggested that this will lead to a

shear zone that penetrates through the entire sample at lower elongations than for a sample which has not been irradiated and combined with coarse slip steps at the surface, will cause reduced ductility [91]. Figure 5.4 highlights a three-grain combination from the irradiated region that exhibits shear transfer (from the dotted box in Figure 5.1d). The grains discussed are labelled G1, G2 and G3 in Figure 5.4a. Grain 2 deforms by prismatic slip but there is a prismatic/pyramidal ambiguity in grains 1 and 3. Strains reach 40% in the centre of grain 1, as illustrated in Figure 5.4b, which is 4 times more than that observed in the non-irradiated grain in Figure 5.3. Only small (<0.5°) deviations from the mean grain orientation are observed in the centre of the grain (Figure 5.4c), in contrast to the nonirradiated grain where domains with rotations of up to 3.5° were observed. Where the channels impinge on grain boundaries, an in-plane rotation relative to the centre of the grain is measured. This is also observed where the slip plane angle changes between grains. Between grains 2 and 3 the slip plane angle changes by 20° and effective shear strain reduces from 35% to 10%. The strain localisation is markedly more diffuse where the slip changes direction in grain 3 and the breadth increases to 1.5 µm. The accumulated strain at the boundary causes a local rotation of up to 4° in grain 3.



**Figure 5.4. Deformation plumes in irradiated grains.** Three grains (G1, G2, G3) exhibiting shear transfer. a) Skeleton map showing average Schmid factor for prismatic slip, overlaid with 90th percentile of effective shear strain. b) Effective shear strain map. c) relative misorientation map. Region taken from dotted box in Figure 5.1d).

In summary, the effect of proton irradiation to ~0.1 dpa on the deformation behaviour of Zircaloy-4 has been investigated using HRDIC after uniaxial tensile deformation along RD to ~2% strain. Effective shear strain was mapped for a non-irradiated and an irradiated region in the same sample, each containing at least 100 grains. Although the strain in the loading direction was 20% lower in the irradiated region, strain heterogeneity, defined as the ratio

of 99.99<sup>th</sup> to 0.01<sup>th</sup> percentile of effective shear strain, was measured to be 6.9 times larger in the irradiated region compared to the non-irradiated region. This is a result of a change in slip characteristics, with the irradiated region exhibiting defined slip bands with low amounts of strain in between compared to more homogenous deformation in the nonirradiated region. The heterogeneous strain behaviour in the irradiated region is most likely due to creation of dislocation free channels by clearing of <a> loops during plastic deformation, which are then subsequently preferred for further dislocation glide. Channels in the irradiated material confine plastic deformation, leading to stress concentrations at grain boundaries. In some cases, local lattice rotations are observed at grain boundaries and in other cases, channels propagate through boundaries. These observations of fundamental differences in the microscopic deformation behaviour of irradiated material will allow validation of plasticity models, which are essential for prediction of irradiated component behaviour.

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### Declarations of interest: None

**Data Availability Statement:** The BSE images used to generate the strain maps, displacement data calculated using LaVision DaVis 8.1.5 and the EBSD data is provided at http://dx.doi.org/10.17632/n4cdwp6pwc.1

### 5.1. Addendum

By comparing the strain localisation at different interrogation window sizes for the nonirradiated and irradiated regions (Figure 5.5a and b), the importance of achieving high spatial resolution to observe the differences in slip behaviour is demonstrated. The difference between the irradiated and non-irradiated regions do not become apparent until an interrogation window size of  $1.25 \times 1.25 \mu m^2$ , at which only the channels showing the largest strains can be clearly observed. The 78 x 78 nm<sup>2</sup> spatial resolution also allows the influence of small (~300 nm) SPPs on effective shear strain to be resolved. Smaller interrogation window sizes will also increase the amount of heterogeneity measured and it is therefore important to take care when comparing data with different spatial resolution and always quote the spatial resolution. For an interrogation window size of 5 x 5  $\mu m^2$ , maximum local strains in the non-irradiated region are around twice the average. This is similar to the heterogeneity measured in previous studies by Padilla et al. [65] and Héripré et al. [185], who measured maximum local strains of ~ 2-4 times the average. For the irradiated region at 78 x 78 nm<sup>2</sup> resolution, the maximum strain is ~20 times the mean.



**Figure 5.5.** Effective shear strain maps and statistics for the a) non-irradiated and b) irradiated regions for interrogation window width of 5.0  $\mu$ m, 1.25  $\mu$ m, 313 nm and 78 nm.

Table 5.2 compares effective shear strain values measured for different hexagonal close packed (hcp) materials. The non-irradiated and irradiated Zircaloy-4 in this study is compared to ZIRLO [238] (another commercial zirconium alloy), magnesium alloy AZ31 [167] and titanium alloy Ti-6AI-4V [172]. The heterogeneity values (defined here as the ratio between the 99.9<sup>th</sup> percentile (P<sub>99.9</sub>) and the mean) are similar for ZIRLO and Zircaloy-4. Irradiation increases the heterogeneity significantly, as discussed in the manuscript. Even though a larger interrogation window size was used, the deformation of heavily textured AZ31 and randomly textured Ti-6AI4V is more heterogeneous than that of moderately textured zirconium alloys.

Material	Texture	Interrogation	P <sub>0.1</sub>	Mean	P <sub>99.9</sub>	P <sub>99.9</sub> /Mean
	(maximum mud)	window size (nm)	(%)	(%)	(%)	
Zircaloy-4	Split-basal (7)	78	0.10	2.39	13.02	5.45
Irradiated	Split-basal (7)	78	0.03	1.94	42.17	21.74
Zircaloy-4						
<b>ZIRLO</b> [238]	Split-basal (5)	117	0.21	3.62	13.86	3.83
			0.49	6.97	32.41	4.65
<b>AZ31</b> [167]	Basal (12)	170	0.66	4.04	65.55	16.23
<b>Ti-6Al-4V</b> [172]	Random (1.3)	116	0.03	2.01	30.62	15.23
			0.06	3.21	43.10	13.43

**Table 5.2.** Comparison of strain heterogeneity across different hcp materials.

Figure 5.6 shows a comparison of the rotation about the z-axis (out of the page) determined from DIC (Figure 5.6b) and from EBSD data (Figure 5.6d) for the grain also analysed in Figure 5.3. By changing the DIC reference frame such that the x-axis follows the slip trace, the lattice rotation can be extracted from material rotation maps. This procedure is described in more detail in [186,243]. For the primary slip trace direction (s<sub>1</sub>), this is illustrated in Figure 5.6c. The same procedure was also followed for the secondary slip trace direction (s<sub>2</sub>) and this is shown in Figure 5.6e. Together, these give reasonably good agreement with the EBSD derived lattice rotation (Figure 5.6d).



**Figure 5.6.** a) Effective shear strain map, b) DIC-derived material rotation map, c) DIC-derived lattice rotation for primary slip trace direction  $s_1$ , d) EBSD-derived lattice rotation map, e) DIC-derived lattice rotation for secondary slip trace direction  $s_2$ .

# 6. The effect of loading direction on slip and twinning in an irradiated zirconium alloy

<u>R. Thomas<sup>1</sup></u>, D. Lunt<sup>1</sup>, M.D. Atkinson<sup>1</sup>, J. Quinta da Fonseca<sup>1</sup>, M. Preuss<sup>1</sup>, F. Barton<sup>2</sup>, J O'Hanlon<sup>2</sup>, P. Frankel<sup>1</sup>

<sup>1</sup> School of Materials, University of Manchester, Manchester, UK.
 <sup>2</sup> Rolls-Royce Plc, Derby, UK.

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# **Contribution statement**

The experiment and proton irradiation campaign were designed by R. Thomas with input from supervisors, P. Frankel and M. Preuss. Sample preparation was carried out by R. Thomas. Data collection on the SEM was primarily carried out by R. Thomas with assistance from D. Lunt. Data analysis and figure generation was performed by R. Thomas using baseline scripts written by M. Atkinson. Material and industrial support was provided by F. Barton and J. O'Hanlon on behalf of Rolls-Royce Plc. The first draft was written by R. Thomas with comments and revision by other authors.

# Abstract

In this study, deformation experiments together with high resolution digital image correlation (HRDIC) were used to quantify the effect of proton irradiation on strain localisation in Zircaloy-4 loaded along the rolling and transverse directions. Significant increases in strain heterogeneity were measured in the irradiated material compared to the non-irradiated material. This was a result of confinement of slip to channels in the irradiated material, which contain high effective shear strain values, with almost no strain in the regions between channels. The active slip systems in the material were also

determined by comparing experimental slip trace angles from HRDIC with theoretical slip trace angles determined using grain orientation from electron backscatter diffraction. An increased amount of pyramidal and wavy basal slip, as well as tension twinning, were observed in the sample loaded along TD, compared to the sample loaded along RD, due to crystallographic texture. No significant change in slip system activity was observed as a result of 0.1 dpa proton irradiation, despite the dramatic change in slip pattern. The findings provide further insight into the role of irradiation on deformation behaviour and provide quantitative data on slip system activation, for as-received and irradiated Zircaloy-4, against which to validate models.

## **Keywords**

zirconium, Zircaloy-4, proton irradiation, plasticity, dislocation channelling, HRDIC, EBSD, slip system

## Introduction

During service, zirconium alloys are subject to neutron irradiation which is known to increase yield stress and decrease ductility as a function of fluence [11,12]. For neutron fluences of  $< 5x10^{25}$  n m<sup>-2</sup>, transmission electron microscopy (TEM) investigations indicate the presence of <a> type dislocation loops on prismatic habit planes [79]. These act as obstacles to dislocation glide during plastic deformation and are responsible for the increased yield stress of irradiated material [41,87]. When a sufficient stress is applied, plasticity-related dislocations can annihilate or drag these irradiation-induced loops, causing thin channels that are cleared or partially cleared of defects [89,92]. Subsequently, these channels act as further dislocation glide paths leading to regions of highly localised plastic deformation [24,41]. The interaction of these highly localised slip regions with constraint of surrounding grains produce strain incompatibilities which exemplify internal stresses. Onimus et al. [244] suggested that the propagation of channels between grains would then be promoted, which could lead to early specimen scale localisation and thus a reduction in ductility.

Previous studies have been successful in using TEM to investigate the mechanism of dislocation channelling on the microscopic scale [41,89]. Nevertheless, complementary techniques such as high resolution digital image correlation (HRDIC) allow deformation behaviour at well below the sub-grain scale to be studied over a large number of grains [166,167,172,174,216]. The basic principle of the technique is the tracking of unique features from images acquired during deformation compared to the original state. To do this, the images are divided into a grid of interrogation windows, containing sufficient features to unambiguously identify each one, and by comparing them before and after deformation the relative displacements for each window can be calculated to provide a full-field displacement map [166]. The desired in-plane strain tensor can then be computed by differentiating the respective displacement field [174]. By combining HRDIC with electron backscatter diffraction, the strain values measured can be related to the microstructure [172]. Additionally, the active slip systems can be determined using slip trace analysis [230]. Such quantitative data can also be used to validate crystal plasticity simulations.

In hexagonal close packed (hcp) materials, the possible slip systems are not symmetrically distributed, have differing strengths and since slip is more difficult along <c+a> compared to <a>, twinning competes with slip for certain deformation conditions [16]. As a result, deformation mechanisms in hcp alloys are complex and not fully understood, especially after irradiation. In commercially pure zirconium deformed at room temperature, Gong et al. [51] determined the critical resolved shear stress for prismatic <a>, basal <a> and pyramidal <c+a> to follow the ratio 1:1.3:3.5. It is generally agreed that prismatic <a> slip is the easiest to activate in zirconium alloys up to around 500°C [16]. However, the formation of a crystallographic texture during processing means the active slip systems will also depend on loading direction. Grains with their c-axis perpendicular to loading direction are referred to as 'soft' grains, since easy prismatic <a> slip is favourable in these grains. Grains with their c-axis parallel to loading direction are referred to as 'hard' grains and are more favourably orientated for slip with a <c> component, such as pyramidal <c+a> slip. Additionally, tension twinning can operate in such grains, of which {10-12}<-1011> are most common for a tensile stress along the c-axis [16].

Due to the time consuming and expensive nature of producing and handling neutron irradiated samples, proton irradiation is increasingly used as a surrogate to investigate the effect of irradiation damage in zirconium alloys [34,80,99,100]. Proton irradiation experiments can also be carried out much more quickly with more precise control of experimental conditions than in a reactor. However, due to the strong interaction of protons with matter, the proton-irradiated volume is confined to a thin region near the surface of the sample, the size of which is defined by the proton energy. It is worth pointing out that previous work in [80,96] has demonstrated that when using appropriate conditions, the density and size of <a> loops produced by proton irradiation in zirconium is consistent with those produced by neutron irradiation. Further, Zu et al. [103] determined similar hardness values from proton and neutron-irradiated Zircaloy-4, at a dose of ~ 2 dpa while Fournier et al. [96] have shown dislocation channelling with similar appearance and width to those observed in neutron irradiated material when deforming proton-irradiated Zircaloy-4.

Since HRDIC measures displacement at the sample surface, it is particularly useful in studying ion irradiated material, where damage is localised near the surface. This was demonstrated previously by the authors in proton irradiated Zircaloy-4, where large strain localisations were observed as a result of irradiation [245]. In the current study, we have addressed the response in more detail by incorporating an intermediate deformation step to capture the development of slip, twinning and channelling. Furthermore, by loading a sample along the transverse direction, channelling behaviour was studied in grains favourable for basal slip. Importantly, the same experiments were performed on non-irradiated material, thereby giving an accurate assessment of the impact of irradiation and loading direction on deformation behaviour in zirconium alloys.

# **Experimental Method**

## Material

The material in this study is a 5 mm thick plate of recrystallised Zircaloy-4, nominally Zr-1.5Sn-0.2Fe-0.1Cr (wt%) [239], supplied by Rolls-Royce plc. Electrical discharge machining (EDM) was used to extract microtensile specimens with a 26 mm gauge length, 3 mm gauge width and final thickness of ~1 mm. Two specimens were machined, one with the rolling direction in the tensile direction and the other with the transverse direction in the tensile direction, hereafter referred to as samples 'RD' and 'TD', respectively. The samples were ground to remove the recast layer from EDM, before diamond polishing and finally hand polished on a MetPrep TruNoire cloth with 0.06 µm colloidal silica solution, diluted with 20% hydrogen peroxide, for ~ 30 minutes.

## Irradiation

The central 5 mm of the specimens' polished surface were irradiated at 344  $\pm$  7 °C simultaneously at the Dalton Cumbrian Facility's 5 MeV tandem pelletron ion accelerator [198], using 2 MeV protons and a current of 16.6  $\mu$ A cm<sup>-2</sup>. Calculations using the 'Quick Kinchin-Pease' method in SRIM 2013 [101] suggest a fairly uniform damage up to ~20  $\mu$ m, with a peak damage at 28  $\mu$ m as illustrated in Figure 6.1. This means that for an average grain diameter of 9  $\mu$ m, approximately 2 grains are sampled in the plateau of the irradiated region. The damage level in this plateau region is ~0.1 dpa. While this damage level is

relatively low, it has been shown to be sufficiently high to result in dislocation channelling during deformation [89]. As suggested by Was et al [75], the proton irradiation was carried out at a higher temperature than typical reactor operating temperatures to allow more diffusion to occur to counteract the shorter irradiation time. These conditions have also been shown to produce microstructures representative of neutron irradiation both in terms of damage features [84] and chemical segregation [34,80]. After irradiation, the samples were OPS polished for 20 minutes to remove around 0.5  $\mu$ m which was sputtered and oxidised during irradiation.



*Figure 6.1.* Damage in displacements per atom as a function of depth for 2 MeV protons in zirconium, calculated using the quick Kinchin-Pease method in SRIM 2013.

Microhardness profiling was performed along the length of the samples using a Struers Durascan 80 hardness tester with a 50 g load. Indents were placed at 250  $\mu$ m intervals approximately 300  $\mu$ m from the edge of the sample. The maximum depth of indents was ~3  $\mu$ m, therefore the plastic zone ahead of the indent should be largely confined to the plateau region in the damage profile. Fiducials for the HRDIC region were placed near the centre of the (5 x 3) mm<sup>2</sup> irradiated region and the non-irradiated region was placed about 2 mm away from the edge of the irradiated region.

### Patterning

Image correlation requires a suitable pattern with unique features that can be tracked before and after deformation. In this study, a pattern of gold speckles was applied to the surface of the sample using the styrene-vapour assisted gold remodelling technique [167]. Initially, a thin gold layer was sputtered onto the polished sample surface using an Edwards S150B sputter coater at a sputtering rate ~ 5-8 nm/min for 5 minutes, equating to a film thickness of ~ 25-40 nm. The sample was then placed on a hot plate at 150°C and exposed to a styrene vapour to remodel the gold from an uniform layer to distinct speckles. In this experiment, a suitable pattern consisting of speckles with diameter of ~20 nm was obtained after three days of remodelling. A more detailed description and schematic of the experimental set-up is given in [167] along with further optimisation of the remodelling process for zirconium alloys in [238].

## Microscopy

For HRDIC, strong contrast between the gold speckles and the zirconium substrate is obtained using backscatter electron imaging (BSE) on a FEI Magellan Field Emission Gun (FEG)-SEM, at an accelerating voltage of 5 kV, with a 2 kV stage bias at a beam current of 0.8 nA at a working distance of 3.4 mm. These conditions were used in immersion mode to enable individual gold speckles to be clearly defined compared to the substrate. This mode uses a magnetic immersion lens to reduce the probe size and reduce aberrations [246]. Small (~5  $\mu$ m diameter) indents placed adjacent to the HRDIC regions were used as fiducials for quickly and accurately relocating the regions. The images for HRDIC were acquired with a horizontal field width (HFW) of 10  $\mu$ m at a resolution of 2048 x 1768 pixel<sup>2</sup> (such that the speckles were on average ~3 pixels wide), and a dwell time of 3  $\mu$ s. In order to study a statistically relevant area, an array of 24 x 24 images<sup>2</sup>, was captured using FEI MAPS with a three-point focus interpolation to ensure accurate focus across the entire region of interest. The images for each deformation step were stitched together using the Grid/Collection stitching function in ImageJ [205] with a linear blend applied prior to performing image correlation.

Grain orientation maps of the HRDIC regions were obtained using a Tescan MIRA3 FEG-SEM equipped with an AZtec electron backscatter diffraction (EBSD) system and an Oxford Instruments Nordlys II detector, at an operating voltage of 20 kV. Macrotexture EBSD analysis was performed before deformation in an area larger than the HRDIC maps (0.4 x 0.3 mm<sup>2</sup>) to measure the texture of the material. More detailed post deformation microtexture EBSD analysis was performed in the HRDIC areas, at a step size of 0.2  $\mu$ m, to enable the strain interactions at the grain boundaries to be analysed further. Relative misorientation maps were plotted to show the angular deviation from the average grain orientation.

#### **Deformation and image correlation**

Ex-situ uniaxial tensile deformation was carried out, at room temperature, using a Kammrath-Weiss 5 kN microtester at an initial strain rate of  $1.6 \times 10^{-4} \text{ s}^{-1}$ . Deformation was interrupted and the sample was unloaded at three plastic strain steps (0.5%, 1.2% and 2.2%) for the TD sample to capture the onset of twins and at two plastic strain steps (1.2% and 2.2%) for the RD sample. Stress strain data and the plastic strains at which DIC images were taken are shown in Figure 6.3b. SEM Images of the HRDIC regions were acquired following each deformation step and were shift corrected relative to the undeformed image to remove any rigid body translation or rotation. HRDIC analysis was then performed, relative to the undeformed image, using the commercially available LaVision Davis 8.4 software [247], using a Fast Fourier Transform (FFT) correlation index. It is performed iteratively, starting with an initial interrogation window size of 1024 x 1024 pixel<sup>2</sup> down to a final interrogation window size of 16 x 16 pixels<sup>2</sup> (with a 0% overlap), at which point 5 iterations are carried out to provide a high accuracy displacement field.

#### Data analysis

The in-plane displacement vector field (u,v,0) was then exported from Davis and imported into an in-house Python routine, utilising the NumPy numerical library [240]. By differentiation of the in-plane displacement field, the components of the strain tensor were determined. The strain in loading direction is given as  $\varepsilon_{xx} = \frac{du}{dx}$ , the strain in normal direction as  $\varepsilon_{yy} = \frac{dv}{dy}$  and the in-plane shear as  $\varepsilon_{xy} = \frac{du}{dy} + \frac{dv}{dx}$ . In order to better visualise the data, effective shear strain is used [167,174] and is given as:

$$\gamma_{\text{eff}} = \sqrt{\left(\frac{\varepsilon_{\text{xx}} - \varepsilon_{\text{yy}}}{2}\right)^2 + \left(\frac{\varepsilon_{\text{xy}}}{2}\right)^2} \,. \tag{17}$$

This measure interprets all strains as shear strains and is therefore a good scalar representation of local deformation at sub-micron scale since most room temperature deformation occurs by shearing of the lattice [174]. The Matplotlib library [241] was used for visualisation of this measure and generating plots.

Homologous points in the HRDIC data and the EBSD data were used to calculate an affine transform, which was applied to the EBSD map to align the two data sets. The active slip system in each grain was then determined by comparing the experimentally determined slip trace angle from HRDIC with all possible slip trace angles calculated using grain orientations obtained by EBSD [230]. The slip planes considered were basal (1), prismatic (3) and first-order pyramidal (6). It should be noted that using this technique it is not possible to differentiate between pyramidal <a> and pyramidal 1st order <c+a> as they provide the same slip trace angle of ±5 degrees was chosen and if more than one slip system lies within this criterion this grain is disregarded from any further slip system analysis.

### Results

### **Material characterisation**

Figure 6.2a shows an EBSD map of the as-received material in IPF (inverse pole figure) RD colouring. The grains in the material are equiaxed, with an average grain diameter of  $9 \pm 4$   $\mu$ m. Stereographic pole figures of {0001}, {11-20} and {10-10} for ~1400 grains are shown in Figure 6.2b. These show a 'split-basal' texture, where basal poles preferentially orient in ND with a spread of ± 28° towards TD while there is also a preferred orientation for one of the {10-10} poles along RD. The basal pole Kearns texture factors were measured to be 0.06, 0.25 and 0.69 for RD, TD and ND respectively. The material also contains second phase particles (SPPs) with composition Zr(Fe,Cr)<sub>2</sub> identified using EBSD. Particle sizes of up to 600 nm were measured, with a total area fraction of ~0.6%. The as-received material was

measured to have <15 wppm hydrogen by inert gas fusion measurement. Following irradiation and gold patterning, a small amount (<0.1% area fraction or <15 wppm) of hydride-like features were observed in BSE imaging, suggesting that a small amount of hydrogen ingress may have occurred as a result of the elevated temperature during patterning or hydrogen implantation from the proton irradiation.



**Figure 6.2.** a) EBSD map for the material investigated. b) EBSD-generated {0002}, {11-20} and {10-10} pole figures for the material investigated (also includes individual grains in white). c) Schmid factors for basal <a>, prismatic <a>, pyramidal <a> and pyramidal <c+a> slip for loading along RD and TD.

Using the same EBSD data, Schmid factor distributions were calculated for basal <a>, prismatic <a>, pyramidal <a> and pyramidal <c+a> slip, assuming local stress is equal to farfield stress. This data is shown in Figure 6.2c, for loading along both RD and TD. These results show that from geometric considerations, prismatic and pyramidal slip are favourable when loading along RD, due to the presence of 'soft' grains with their c-axes aligned perpendicular to the loading direction. When loading along TD, the average Schmid factor for basal <a> slip is higher than for loading along RD, since basal poles are preferentially oriented ~30° towards TD. Twinning would be expected for 'hard' grains which have their c-axis aligned close to the loading direction, as is the case for some grains in the sample loaded along TD. This is illustrated by the points in the {0002} pole figure (Figure 6.2b), which shows that there are more grains near the TD poles compared to the RD poles.

#### Macroscopic deformation behaviour

Hardness measurements taken along the edge of the TD sample are reported in Figure 6.3a. The uncertainty on these measurements was estimated using the standard deviation of measurements in the non-irradiated region. The baseline hardness of the material was 200  $\pm$  12 0.05HV and hardness in the irradiated region was 245  $\pm$  17 0.05HV, which corresponds to a hardness increase of 23% due to irradiation. For the RD sample, the baseline hardness was measured to be 204  $\pm$  16 0.05HV and the hardness in the irradiated region was 245  $\pm$  17 0.05HV.

The stress-strain curves obtained for both RD and TD samples are shown in Figure 6.3b, where strain was calculated from crosshead displacement. Compliance in the tester means the elastic portion of the curve does not represent the actual elastic response of the material. The 0.2% offset proof stress was measured to be ~350 MPa and ~450 MPa for loading along RD and TD respectively. These values will contain a contribution from the non-irradiated and irradiated regions of the tensile specimen, however the majority (80%) of the specimens was not irradiated. Therefore, the values measured here are similar to those measured by Mozzani et al. [248] in non-irradiated Zircaloy-4. Figure 6.3b also shows different strain hardening behaviour in the samples, with a larger strain hardening rate and lower yield stress in RD.



**Figure 6.3.** a) Sample schematic with irradiated region highlighted with microhardness profile along edge of TD sample. b) Stress-strain curves for TD and RD microtensile specimens, generated from cross-head displacement.

#### **HRDIC uncertainty and mesoscopic strain**

An image of the pattern used for HRDIC is shown in Figure 6.4a with a grid to illustrate the interrogation window size used for correlation in red. By imaging the same region twice successively with no deformation and performing a correlation, the uncertainty on measurement of strain was calculated. The data is presented as a histogram in Figure 6.4b, which shows a normal distribution with a mean of ~0%. The breadth of the distribution depends on the imaging conditions chosen, such as dwell time and interrogation window size. For this study, the uncertainty in the measurement of strain in loading direction for a single pixel from HRDIC with a 68% confidence interval is  $\pm 0.23\%$ .

The average strain in the loading direction (calculated from HRDIC) for each region and deformation step is plotted in Figure 6.4c. This can be thought of as equivalent to having a strain gauge of width ~200  $\mu$ m attached to each region. Since the irradiated region has a higher yield stress due to prismatic <a> loops and is strained in series with the non-irradiated region, a lower plastic strain was measured in the irradiated regions compared to the non-irradiated regions. This agrees with finite element calculations of strain measured in Zircaloy-4 by Fournier et al. [96], which suggest that the thin hardened layer in the proton irradiated region reinforces the centre of the specimen.

With each deformation step, the relative difference in strain between the irradiated region and non-irradiated region becomes smaller. At the strains examined here, the non-
irradiated region will have a positive work hardening rate. However, macroscopic plastic instability begins near yield in Zircaloy-4 irradiated with neutrons to the same dpa as in this study and a negative work hardening rate is observed. As a result, the strains for the nonirradiated and irradiated regions converge with increasing deformation.

The strain in the irradiated region, relative to the non-irradiated, is higher for the RD sample compared to the TD sample. This may suggest that the slip systems activated in the TD sample are more strongly affected by irradiation than those in the RD sample. Macroscopic plastic instability at yield may also cause heterogeneity at scales larger than the HRDIC region and since the RD and TD samples are separately deformed, the choice of region may account for some of the differences in average strain observed between the irradiated regions.



**Figure 6.4.** a) Magnified BSE image of the speckle pattern b) Measurement of uncertainty in HRDIC strain measurement c) Comparison of average strain in loading direction measured from HRDIC at each strain step for the TD and RD samples in the non-irradiated and irradiated regions.

# Sub-grain scale strain localisation

For clarity, Figure 6.5 shows an effective shear strain map of a quarter of the total HRDIC region for each condition at macroscopic strains of ~1.2% and ~2.1%. Grain boundaries from post-deformation EBSD have been overlaid onto the strain maps in white. It should be noted that twins that have not yet nucleated are present in the grain boundary map for the first strain step since EBSD was only acquired after the final deformation step. The critical misorientation for the definition of a grain boundary was chosen to be 4°, as the

strong crystallographic texture across the material means grain boundary misorientations can be small. The mean strain in loading direction is also noted for each condition.

Comparing Figure 6.5a with Figure 6.5b shows the extent of plastic strain localisation due to irradiation. Distinguishing individual slip bands in the non-irradiated material is difficult since slip is diffuse, whereas channelling in the irradiated region causes more planar slip. Similar observations can be made on the TD sample by comparing Figure 6.5c with Figure 6.5d, where slip is more heterogeneous in the irradiated region. Twinning is present in both TD regions, denoted by red dotted boxes. These are characterised by thick bands with a uniform effective shear strain, which increase in width with increasing strain. In both non-irradiated and irradiated regions, the amount of effective shear strain within twins is similar, around 4-7% in the first step and 7-10% in the next.



**Figure 6.5.** Effective shear strain maps after macroscopic strain of 1.2% and 2.1% for the a) nonirradiated RD, b) irradiated RD, c) non-irradiated TD and d) irradiated TD. Grain boundaries from post-deformation EBSD are overlaid in white and twins are highlighted by dotted red boxes.

The number of active slip systems identified in a grain is also given in Table 6.1a-c. In the >80% of cases in all regions, a single slip plane was active. The proportion of grains with two or more active slip systems increased with irradiation. Three slip systems were identified in two grains in each of the non-irradiated TD and irradiated TD regions. Three of these four grains had their c-axis aligned within 25 degrees of TD and all four grains are thought to have deformed along multiple pyramidal slip planes. No grains are present with their c-axis aligned within 25 degrees of grains which deform by more than two slip planes in the sample deformed along RD.

	a) Single active	b) Two active	c) Three active		
	slip system	slip systems	slip systems		
RD	131 (87.3%)	19 (12.7%)	0		
RD irradiated	173 (82.4%)	37 (17.6%)	0		
TD	122 (87.1%)	16 (11.4%)	2 (1.4%)		
TD irradiated	143 (82.2%)	29 (16.7%)	2 (1.1%)		

Table 6.1. Summary of the amount of slip systems active in each grain, for each region.

Figure 6.6 show maps of maximum Schmid factor for prismatic and pyramidal slip based on average grain orientation for the same maps shown in Figure 6.5 (which are each a quarter of the total area analysed). Red points are overlaid to indicate regions where the effective shear strain is greater than the 95th percentile at the final deformation step. These maps further illustrate the diffuse nature of slip in the non-irradiated region. High strain values in the irradiated region are almost exclusively contained within planar slip bands in the sample loaded along RD. In the case of the TD sample, some grains have a low Schmid factor for basal and prismatic slip. Grains which are black (Schmid factor <0.1) are less likely to contain high strain values due to slip, but relatively large strains due to twinning are present (highlighted in green). In fact, the majority of data points from within twins are in the 95<sup>th</sup> percentile. It is also apparent from this map that grains adjacent to twins are likely to have areas of high strain either due to slip bands (where slip Schmid factor is high) or further twins (where slip Schmid factor is low). Propagation of channels between multiple grains can be readily observed in the irradiated region. These are more difficult to observe



in the non-irradiated region due to the significantly finer slip bands, which are not individually resolved.

**Figure 6.6.** Maximum Schmid factor for prismatic and basal slip based on average grain orientation for a) non-irradiated RD, b) irradiated RD, c) non-irradiated TD and d) irradiated TD. Grain boundaries from post-deformation EBSD are overlaid in black, 95th percentile of effective shear strains at ~2.1% macroscopic strain are overlaid in red and twins are highlighted by dotted green boxes. White dotted boxes are regions investigated in detail later.

#### Strain frequency distribution

Whilst qualitative observations of the different deformation characteristics can be made from the strain maps, the difference in strain heterogeneity can be further highlighted and compared quantitatively by plotting frequency distributions of the effective shear strain (Figure 6.7). To compensate for the slight differences in the applied strain between regions, the effective shear strain values have been normalised by dividing them by the average effective shear strain in each region. To highlight the differences at both low and high strain, the data has been plotted on a log-log scale. The 0.01th and 99.99<sup>th</sup> percentile are also noted for each dataset. These values have been used instead of the minimum and maximum to exclude any effect of noise from single pixels of high or low strain. Irradiation causes the 99.99<sup>th</sup> percentile effective shear strain values to significantly increase in all cases. This is attributed to the dislocation channelling mechanism, resulting in further deformation becoming easier within the channels, compared to the regions where irradiation-induced dislocations remain, thus increasing the heterogeneity. This can be seen visually in Figure 6.5. For low strains, at normalised effective shear strains of less than ~0.7, the frequency is higher for the irradiated data compared to the non-irradiated data. This is likely to be a result of the areas outside the dislocation channels in the irradiated region accumulating very little deformation due to the channels acting as easy paths for slip. Higher 99.99<sup>th</sup> percentile values are also measured for the TD samples compared to the RD samples.



**Figure 6.7.** Effective shear strain histograms for specimens loaded along TD and RD, for nonirradiated and irradiated regions, at a) 1.2% and b) 2.1% macroscopic strain. Arrows point to 0.01th and 99.99<sup>th</sup> percentile strains to highlight the increased localisation in irradiated samples.

#### Slip system activity

Slip system activity was calculated for each deformation steps and the results are displayed in Figure 6.8. In 20-50% of cases, a unique solution for the slip plane was not identified and these results are excluded from the analysis. In the first deformation step for the irradiated TD sample, only 0.1% strain was recorded for the region and as a result only 15 grains were observed to have dislocation channels. The uncertainty is therefore larger for these results. With increasing strain, a reduction in the proportion of grains which deform by prismatic slip and an increase in the proportion of grains which deform by pyramidal slip was observed. Similar proportions of basal and an increase in the proportion of twinning were observed with increasing strain. The majority of deformation in the RD samples occurs by prismatic slip, 96% and 87% for as-received and irradiated, respectively. The remainder was pyramidal slip, with the exception of one grain which deformed by basal slip in the irradiated region. In the TD sample; prismatic, pyramidal and basal slip; as well as {10-12}<-1011> twinning were observed. Comparing TD at 0.4% strain to TD irradiated at 0.4% strain, a small increase in the proportion of grains which deform by pyramidal slip was measured as a result irradiation. However, no significant change in slip system activation was observed.



*Figure 6.8.* Progression of slip system activation for RD (non-irradiated), RD (irradiated), TD (non-irradiated) and TD (irradiated) regions at macroscopic strains of 1.3% and 2.2%.

The inverse pole figures (IPF) in Figure 6.9a-d, show slip system activity, determined from slip trace analysis, for each region, as a function of grain orientation relative to loading direction. Grains which did not deform, or for which the slip system could not be identified are also shown in grey. These are distributed evenly over the IPF, suggesting they are not of a particular slip system type. Therefore, only considering cases with a unique solution should give representative proportional slip activity. For the sample loaded along RD, no grains are present which have their basal poles oriented within 35° of the loading directions. Therefore, the Schmid factor for {10-12}<-1011> tension twinning is <0.025, as shown in Figure 6.9e and no twinning would be expected. This agrees with experimental observation. For the sample loaded along TD, the orientation of grains relative to loading is more homogeneous, since the split-basal texture is spread away from ND and towards

TD. As a result, there are grains oriented with their basal poles close to the loading direction. In some of these grains, twinning is observed, all of which are tension twins {10-12}<-1011>, with a characteristic 85° misorientation measured between parent and twin with EBSD.

The distribution of maximum Schmid factors for each activated slip plane, grouped by type of plane (basal, prismatic and pyramidal), is also shown in Figure 6.9. In every region, the minimum Schmid factor for each activated slip plane type is lowest for prismatic (0.26 to 0.32), compared to basal (0.42 to 0.44) and pyramidal (0.38 to 0.42). This suggests that in this study, the prismatic slip system remains the easy slip system, for both loading directions, including after irradiation. The ratio between the Schmid factor of the lowest activated prismatic system to the Schmid factor of the lowest activated basal system was 1.6 for both non-irradiated and irradiated regions of the TD sample. This is consistent with a previously reported ratio of 1:1.33 for the CRSS of the prismatic:basal slip system by Gong et al. [51] and the difference is likely to be due to the assumption of far-field stress in this study.



**Figure 6.9.** Active slip system after ~2.1% strain, plotted on a stereographic IPF, where crystal orientations are relative to the loading direction and distribution of Schmid factors for activated slip systems for samples loaded in a) RD (non-irradiated), b) RD (irradiated), c) TD (non-irradiated) and d) TD (irradiated). e) Schmid factor for basal <a>, prismatic <a>, pyramidal <a>, pyramidal <c+a> and {10-12} tension twinning plotted on an IPF, where crystal orientations are relative to the loading direction.

## Discussion

#### Macroscopic response

Irradiation damage can lead to significant changes in mechanical properties, even at low doses. This has been demonstrated by Farrell et al. [89] where a steep decrease in elongation to failure as a function of dose was measured between non-irradiated and 0.01 dpa neutron irradiated Zircaloy-4. Prompt necking at yield was also observed at 0.01 dpa and at higher doses a more gradual decrease in ductility was measured. It should be noted that a conversion of  $6 \times 10^{24}$  n m<sup>-2</sup> dpa<sup>-1</sup> was applied in the study to convert neutron fluence to dpa. At a dose of 0.1 dpa the elongation to failure was measured to be 17%, compared to 35% in the non-irradiated material. An inverse trend was observed in the yield stress, with a steep increase in yield stress up to ~0.01 dpa. Following 0.1 dpa neutron irradiated material. These observations were made on samples irradiated at 65-100°C, however a study by Higgy and Hamad [249] suggests that irradiation at 320-360°C lowers the damage level at which the hardening rate begins to plateau.

In light of the significant changes in macroscopic performance of alloys irradiated to low doses, proton irradiation to a damage level of ~0.1 dpa was carried out in this study. The macroscopic response of the non-irradiated and irradiated regions was compared by performing microhardness along the edge of the samples. An increase in hardness of 23% was observed in the region subject to 0.1 dpa proton irradiation, compared to the non-irradiated region. Zu et al. [250] measured a similar increase in hardness in 2 dpa proton-irradiated Zicaloy-4. More recently, Yang et al. [251] performed nanoindentation on Zircaloy-4 irradiated with Zr ions to 0.1 dpa and 0.2 dpa and found almost identical hardness values for both damage levels. These observations suggest that hardness saturates at an early stage, in agreement with the significant decrease in hardening rate at ~0.1 dpa observed by Higgy and Hammad [249].

#### **Dislocation channelling**

The increase in yield stress of irradiated zirconium alloys is known to be a result of a high density of small <a>-type dislocation loops, acting as obstacles to dislocation glide. When a sufficient stress is applied, these irradiation-induced loops are swept by dislocation glide from plastic deformation. At doses of 0.01 dpa and above, dislocation channelling deformation has been found to be dominant in TEM observations by Farrell et al. [89] in neutron irradiated Zircaloy-4. This is characterised by thin channels (~40-100 nm), which are either partially or fully cleared of irradiation induced loops. The spatial resolution of the HRDIC technique would be sufficient to capture such fine detail, but the bands of shear strain arising from channelling deformation (which are multiple pixels wide) were found to be wider than the channels observed in TEM. Since DIC measures the accumulated strain during deformation, it is possible that this strain field extends beyond the cleared (or partially cleared) channel observed in TEM [245]. The spacings between the channels are consistent with TEM observations [245].

Even though the average strain in loading direction was lower in the irradiated region due to hardening, HRDIC captured significantly larger local strains due to irradiation enhanced strain localisation. This is further illustrated in Figure 6.10a and b, which show effective shear strain maps for a small section of the TD irradiated region. The magnitude of strain in dislocation channels is shown graphically in Figure 6.10c. An average channel width of 250 nm (corresponding to 3 pixels in the DIC map) was measured with a spacing between channels of 1  $\mu$ m for the grains in Figure 6.10. In grain 1, where this profile was measured, the active slip system could not be distinguished between prismatic and pyramidal slip. Grains 2 and 3 deformed by wavy slip, approximately aligned with the basal slip trace. Wavy basal slip, caused by cross-slip between basal and prismatic planes, has been reported in literature by Caillard et al. [252] in an interstitial free zirconium-hafnium alloy using TEM. On closer inspection, the basal slip trace in grain 2 appears to have a second identifiable trace angle aligned with the prismatic\pyramidal plane. As well as the primary basal slip trace, an interesting pyramidal channel is also observed at the 2.2% strain step. Prismatic slip was identified in grain 4 and at the 2.2% strain step, a second prismatic slip system appears to activate. Two slip systems are active in grain 5, the first of which is either prismatic or pyramidal and the second could not be identified and could be explained by second order pyramidal slip. Relative misorientation maps (obtained from EBSD) are shown in Figure 6.10d. Although the average misorientation within grains is low (~0.7°, similar to that observed for the non-irradiated region), values of up to 4° are measured locally in some grains, near grain boundaries. These are associated with strain incompatibility caused by large shear strains within channels impinging on grain boundaries.



**Figure 6.10.** Effective shear strain maps for a small section of the TD irradiated region for a) ~1.2% and b) ~2.2% macroscopic strain. Orientations and slip trace angles for numbered grains are displayed beneath. c) Line profile of strain along white arrow in a) & b). d) Relative misorientation map from EBSD with arrows highlighting highest values.

#### Slip system activity

The key advantage of the HRDIC-based slip trace analysis, is that many more grains can be sampled compared to TEM-based studies, which typically look at 10-50 grains per sample [41,96]. In cases where prismatic and pyramidal slip planes are close together, distinguishing between them can sometimes be challenging in TEM-based studies (~10% ambiguity in the axial sample of Onimus et al. [41]). However, this was also an issue HRDIC

studies, where an ambiguity existed in ~40% of cases. This was exemplified by the angular acceptance criteria of  $\pm 5$  degrees, which may be pessimistic, given the accurate alignment which can be achieved between the EBSD and HRDIC datasets. An additional complication in TEM-based studies is the need to tilt the sample to achieve an appropriate imaging condition. Even with a large angular domain double-tilt holder, some basal channels in samples loaded along the transverse direction could not be observed [41]. In Table 6.1, the results from slip trace analysis for this study are compared to previous studies.

## Slip system activity in RD

In the current study, the active slip systems in non-irradiated material deformed along RD were determined to be almost entirely by prismatic <a> slip, following tensile deformation to ~2.6% strain. Previous HRDIC studies by the authors under similar conditions also found primarily prismatic slip in non-irradiated samples deformed along RD at room temperature [245]. This was expected given the low CRSS of prismatic slip in non-irradiated zirconium at room temperature and the texture relative to the loading direction. Comparison of an elastoplastic self-consistent model to neutron diffraction data by Xu et al. [253] predicted accommodation of tensile deformation along RD by both prismatic <a> and basal <a> slip in the early stages of deformation (~380 MPa true stress, corresponding to around 2-3% plastic strain). No tensile twinning was predicted, in agreement with the experimental data here. However, in the current study no basal slip was measured, in contrast to the prediction of significant basal slip by Xu et al. [253]. It should be noted that only a broad agreement between neutron diffraction data was obtained by the model. Also, since the measurements by HRDIC are of the sample surface, compared to neutron diffraction which is a bulk technique, surface effects may also play a role in altering the activated slip systems.

No change in slip system activity was observed as a result of proton irradiation to 0.1 dpa. A previous study by Onimus et al. [41], although carried out at 350°C on sample subject to a much higher irradiation dose, also showed no significant change in slip system activity for deformation along RD. Farrell et al. [89] also observed primarily prismatic slip in neutronirradiated Zircaloy-4 at damage levels up to 0.8 dpa, deformed at room temperature. These agree with the results of the current study, where primarily prismatic and some pyramidal slip was observed.

#### Slip system activity in TD

In the current study, the active slip systems in non-irradiated material deformed along TD were determined to be 50% prismatic <a>, 35% pyramidal, 5% basal <a> and 10% twinning, following tensile deformation to ~2.6% strain. In non-irradiated material, deformed along TD, Regnard et al. [94] observed primarily prismatic slip, with pyramidal <c+a> at higher strains and rarely basal and pyramidal <a> slip. X-ray line broadening analysis by Ungár et al. [95] found primarily <a>-type dislocations (~60%) with some <c+a> component dislocations and very little <c>-type slip in Zircaloy-2 deformed to 15% strain. EBSD slip trace analysis by the same authors showed primarily prismatic slip (in ~50% of grains), some pyramidal and an instance of twinning (in one of 11 grains). The observations made by Ungár and Regnard are similar to those made in the current study. Compression of Zr-1.2wt%Sn at room temperature along RD and TD by Mani Krishna et al. [73] indicate the presence of {10-12}<-1011> tensile twinning, as observed in the current study. Modelling and subsequent comparison to neutron diffraction data by Xu et al. [253] predicts prismatic <a> primarily with basal <a> and some tensile twinning (5%) activation in pure zirconium for deformation along TD. Although the primary slip system agrees with the current study, less basal slip and more pyramidal slip is measured in the current study. It should be noted that pyramidal <a> was not included in the model and could be represented as a combination of prismatic <a> and basal <a>.

Following irradiation by neutrons [41,47] and protons [96], other authors have found almost exclusively basal channelling when deforming along TD at both room temperature and 350°C to macroscopic strains of ~0.5% to damage levels of 1-2 dpa. However, there is some disagreement in literature, where Adamson and Bell only observed prismatic and pyramidal channelling during deformation along TD [93]. In the current study, primarily prismatic slip with some pyramidal slip, basal slip and twinning was observed for non-irradiated material deformed at room temperature along TD. The slip system activity was similar for both non-irradiated and 0.1 dpa proton irradiated material, however a small

increase in pyramidal slip was observed following irradiation. From x-ray line profile analysis studies by Long and Balogh et al. [254,255], significant hardening of prismatic and basal <a> slip was observed in Zr-2.5Nb after neutron irradiation to 0.4 dpa and only a small impact on pyramidal <c+a> slip. This is consistent with the increased amount of pyramidal slip observed in the irradiated material in this study. However, the anisotropy between prismatic and basal slip was found by Long and Balogh et. al to be significantly reduced after 0.4 dpa irradiation, in contrast to this study where no change in relative activation was observed. From a Schmid factor analysis, the prismatic slip system remained the most easily activated slip system om this study. It is therefore probable that basal channelling becomes increasingly probable as dose is increased from 0.1 dpa to 1-2 dpa.

	Study	Irradiation condition	Number of activated slip/twin systems			
	(strain \ temp)					
			Pr	Ва	Ру	Tw
RD (axial)	This study	Non-irradiated	124	0	5	0
	(2.2% \ 25°C)	0.1 dpa proton irradiated	136	1	19	0
	Thomas et al.	Non-irradiated	31	0	2	0
	[245] (2% \ 25°C)	0.1 dpa proton irradiated	31	0	3	0
	Onimus et al. [41]	$12 \times 10^{25}$ n m <sup>-2</sup> (~20 dpa)	14	0	4	-
	(1.6% \ 350°C)	neutron irradiated Zr-1%Nb				
	This study	Non-irradiated	18	1	6	2
TD	(0.4% \ 25°C)	0.1 dpa proton irradiated	40	3	17	4
	Onimus et al. [41]	0.6×10 <sup>25</sup> n m <sup>-2</sup> (~1 dpa)	0	21	0	-
	(0.4% \ 350°C)	neutron irradiated Zircaloy-4				
	Onimus et al. [41]	0.6×10 <sup>25</sup> n m <sup>-2</sup> (~1 dpa)	0	17	0	-
(transverse)	(0.36% \ 350°C)	neutron irradiated Zircaloy-4				
	Fournier et al. [96]	2 dpa proton irradiated	1	10	0	-
	(0.5% \ 350°C)					
	Ungár et al. [95]	Non-irradiated	8	1	6	1
	(15% \ 25°C)					

Table 6.2. Slip system activity determined by this study compared to literature.

## Conclusion

Deformation behaviour in proton irradiated Zircaloy-4 was measured using HRDIC, at uniaxial tensile strains of up to 2.1%, in samples loaded along RD and TD. Each HRDIC region is  $\sim 200 \times 170 \,\mu\text{m}^2$  and contains  $\sim 300-450$  grains. EBSD maps of the same regions were taken to measure grain orientation and theoretical slip trace angles. The active slip system(s) in each grain were determined by comparing these theoretical slip trace angles with experimental slip trace angles from HRDIC. The findings can be summarised as follows:

• Strain heterogeneity is higher in the irradiated material, as a result of confinement of slip to dislocation channels, characterised by slip with high effective shear strains

and relatively large spacings. More diffuse, homogeneous slip was observed in the non-irradiated material.

- When loaded along RD, primarily planar prismatic and some pyramidal slip was observed in both the non-irradiated and irradiated regions. Wavy basal slip arising as a result of cross-slip and {10-12}<-1011> type tension twins were additionally observed in the sample loaded along TD.
- No significant change in slip system activity was observed following proton irradiation to 0.1 dpa. Further systematic studies to determine slip system activity at intermediate damage levels (between 0.1 and 1 dpa) would be worthwhile to determine the threshold for a transition to basal channelling.

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## 6.1. Addendum

The data provided by HRDIC and EBSD provides a wealth of information, all of which could not be fitted into a single manuscript. Some additional preliminary figures are included in this section to illustrate examples of other information that can be determined using a combination of the HRDIC and EBSD techniques.

## **Relative displacement ratio analysis**

Using the relative displacement ratio (RDR) technique proposed by Chen et al. [193], the Burger's vector of the active slip system can be calculated. Additional details of the technique and implementation are in section 3.9.3. To validate the technique, the experimental RDR value was calculated for slip traces determined to be on a prismatic slip plane from traditional slip trace analysis. In this case, only an <a> Burger's vector will exist; therefore, the actual values can be determined using grain orientation obtained from EBSD grain orientation. Comparison between the experimental and the closest calculated value are shown in Figure 6.11. In most cases, a good agreement was found, with 90% of calculated values within 0.3 of the experimental values.

This technique could be particularly useful to identify the slip direction for pyramidal slip planes, where both <a> or <c+a> Burger's vector are possible. Being able to determine this for many grains from HRDIC would be beneficial for comparison with crystal plasticity modelling. Figure 6.12 shows the slip direction measured using the RDR technique for pyramidal slip planes, plotted on an IPF triangle. In some cases, the experimental RDR value was equidistant to both <c+a> and <a> calculated RDR values and were discounted from further analysis and are denoted as ambiguous in Figure 6.12. The data suggests that both <a> and <c+a> Burger's vectors are observed for pyramidal slip. Pyramidal <c+a> is normally observed where the loading direction is close to the <0002> crystal direction, in the region where pyramidal <c+a> slip is geometrically favourable, whereas pyramidal <a> is generally seen otherwise. It is of course possible that the grains which are thought to have deformed by pyramidal <a> have in fact deformed by prismatic <a>. The acceptance

criteria of  $\pm 5$  degrees and the discounting of grains where the slip system was ambiguous should mean that the slip plane determined is correct however.



**Figure 6.11.** Comparison between experimentally determined RDR values for slip traces on prismatic planes, compared to theoretical values determined using EBSD grain orientation for <a> slip directions.



Figure 6.12. Slip direction determined by RDR plotted for grains with pyramidal slip plane

The RDR method has been validated for a limited number of grains using focused ion beam lamellae extraction and transmission electron microscopy for Ti-6Al-4V [256]. Therefore, further investigation on zirconium is required before this observation can be confirmed.

## **Twin formation**

The development of shear strain associated with twin formation can also be measured using HRDIC. Figure 6.13 contains HRDIC maps for small regions of the non-irradiated sample loaded along TD. The grain boundary maps and grain orientations from EBSD are overlaid. Pyramidal slip is observed to be well defined and planar, whereas basal slip is observed to be wavy. The c-axis of Grain A is aligned within 5° of the loading direction and shear along a twinning plane is observed at ~0.4% strain. The shear localisation widens in the following deformation steps. The c-axis of Grain B is ~15° away from the loading direction and as a result, no evidence of twinning is observed in the HRDIC map until ~2.2% strain. In both grains, strain localisation is observed adjacent to the twin, prior to its formation.



**Figure 6.13.** Shear associated with twin formation in Zircaloy-4 measured using HRDIC at three deformation steps, from 0.4% to 1.1% to 2.2% macroscopic strain. Grain boundaries, determined by EBSD after the final loading step, are overlaid in white with twin boundaries in red. Average grain orientations denoted by hcp crystals.

# 7. Effect of hydrides and second phase particles on strain localisation in Zircaloy-4

<u>*R.* Thomas</u><sup>1</sup>, D. Lunt<sup>1</sup>, M.D. Atkinson<sup>1</sup>, J. Quinta da Fonseca<sup>1</sup>, M. Preuss<sup>1</sup>, F. Barton<sup>2</sup>, J. O'Hanlon<sup>2</sup>, P. Frankel<sup>1</sup>

<sup>1</sup> School of Materials, University of Manchester, Manchester, UK.
<sup>2</sup> Rolls-Royce Plc, Derby, UK.

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# **Contribution statement**

The experiment was designed by R. Thomas with input from supervisors, P. Frankel and M. Preuss. Sample preparation and hydriding was carried out by R. Thomas. Data collection on the SEM was carried out by R. Thomas. Data analysis and figure generation was performed by R. Thomas using baseline scripts written by M. Atkinson. Material and industrial support was provided by F. Barton and J. O'Hanlon on behalf of Rolls-Royce Plc. The first draft was written by R. Thomas with comments and revision by other authors.

# Abstract

During service, zirconium alloys pick up hydrogen as a result of corrosion, which leads to the formation of hydrides above the solubility limit for hydrogen at a given temperature. These hydrides can have deleterious effects on mechanical properties, depending on quantity and orientation relative to the loading direction. This study uses a combination of high-resolution digital image correlation and electron backscatter diffraction (EBSD) to quantify the partitioning of strain between the different phases present in hydrided Zircaloy-4. It was found that the average strain within the  $\delta$ -hydride and Zr(Fe,Cr)<sub>2</sub> second phase particles was lower than in the metal, following uniaxial deformation to 3% strain along RD. Shear bands in the zirconium matrix were observed to terminate at the hydride in almost all cases, but some ambiguity exists due to the presence of non-indexed points in EBSD near boundaries. Some diffuse shear was observed in the hydride however suggesting hydrides do accommodate some plastic deformation and second phase particles provide a good comparison given their undeformable nature relative to the matrix. The findings provide further insight into the role of hydrides on deformation behaviour and provide quantitative data on the local strains observed inside and near zirconium hydrides and second phase particles in Zircaloy-4.

## Introduction

Zirconium alloys are widely used by the nuclear industry as fuel cladding in light water reactors. During service, hydrogen is absorbed into the material as a result of corrosion. Since the solubility of hydrogen in zirconium at room temperature is very small, possibly as low as 10<sup>-4</sup> at% (~1 wt%) [123], hydrides are precipitated from supersaturated hydrogen as the material is cooled from operating temperature. For slow cooling rates ( $\leq 10^{\circ}$ C\min), delta zirconium hydrides with a face centered cubic (FCC) crystal structure are predominantly formed [124,145,257]. Transmission electron microscopy (TEM) [159], Xray diffraction [258] and high resolution electron backscatter diffraction [259] have shown precipitation of hydrides to increase dislocation density within and near hydride platelets as a result of the misfit strain between the matrix and delta hydride. These hydrides are generally considered detrimental to fracture strength and ductility for slow strain rates. They are particularly detrimental when they are oriented perpendicular to the loading direction, which can occur when a tensile stress is applied during precipitation [21]. Hydrogen also enables the delayed hydride cracking (DHC) mechanism, whereby hydrides are nucleated at a crack tip as a result of a hydrogen migration due to a hydrostatic tensile stress, leading to sub-critical crack advancement [133].

Due to their FCC structure, slip along {111} planes has been observed in bulk delta zirconium hydride, but only at temperatures above 100°C, below which no plastic deformation occurs [42]. However, in service material, hydrides are the minority phase amongst the zirconium matrix, with hydrogen concentrations reaching up to 600 wppm in high-burn up Zircaloy-4 [260]. Shear bands from the matrix have been observed to terminate at the matrix-hydride boundary by Weekes et al. [159] during micropillar testing, suggesting that the hydrides are strong when the direction of maximum resolved shear is perpendicular to the plane of the microscopic platelets. However, the same study showed that in some cases, slip between the platelets was observed (suggesting that hydrides can deform in the plane of the macroscopic hydrides) and such slip through a hydride platelet has been also been observed using scanning electron microscopy (SEM) by Grange et al. [261]. Few observations have been made of shear bands in hydrided zirconium alloys however and how the hydrides accommodate plastic deformation is still unclear. The

orientation of hydrides is important with regards to deformation and this has been shown to be determined by an orientation relationship of  $\{0001\}_M | |\{111\}_H \& <11-20>_M | |<110>_H$  relative to the zirconium matrix [124,132,139–146]. The relationship is particularly important when considering slip transfer between the hexagonal close packed (HCP) matrix and FCC hydride.

High resolution digital image correlation (HRDIC) gives quantitative local strain maps and is often combined with electron backscatter diffraction (EBSD) to relate microstructure and grain orientation to strain and slip system activity [167,180,193,208,245]. The two techniques have previously not been exploited together to calculate strain partitioning between different phases however. The aim of the current study is to quantify the partitioning of strain between the zirconium matrix, delta hydride and Zr(Fe,Cr)<sub>2</sub> second phase particles (SPP) as a result of deformation, to better understand the role of embedded hydrides on the deformation behaviour of zirconium alloys. Spatially resolved strain data will also allow the investigation of shear within the hydride and at the interfaces.

## **Experimental Method**

#### Material

The recrystallised Zircaloy-4 (nominally Zr-1.5Sn-0.2Fe-0.1Cr wt%) plate used in this study was provided by Rolls-Royce Plc. Texture analysis shows a 'split-basal' texture, with basal poles oriented preferentially in ND with a spread of  $\pm$  28° towards TD. Further details are given in [262], which is based on the same material. Electrical discharge machining was used to extract flat microtensile specimens of 50 mm long in RD, 10 mm wide along the TD and around 1 mm thick, with a gauge width of 3mm, as illustrated in Figure 7.1b. To remove the recast layer, the sample was ground then pickled in a 5% HF, 45% HNO<sub>3</sub>, 50% H<sub>2</sub>O solution for 30 seconds to remove the native oxide layer.

## Hydrogen charging

Hydrogen charging was performed electrochemically, by immersing the sample in a 1N sulphuric acid electrolyte between two platinum electrodes in a glass reaction vessel, as illustrated in Figure 7.1a. By applying a 25 mA cm<sup>-2</sup> current between the sample and

electrodes for 4 days with a Keysight E36104A power supply at room temperature, a hydrogen rich rim was generated on the surface of the specimen. To redistribute hydrogen throughout the sample, a homogenisation heat treatment was carried out at 400 °C for 18 hours in an argon atmosphere, followed by furnace cooling at a rate of ~2 °C min<sup>-1</sup>. The oxidised layer was ground, the sample was polished with diamond paste and finally hand polished with 0.06  $\mu$ m colloidal silica solution (diluted with 20% hydrogen peroxide) for 40 minutes.



*Figure 7.1.* a) Experimental apparatus used for electrochemical hydrogen charging. b) Microtensile sample geometry.

#### Patterning and microscopy

The styrene assisted remodelling technique [167,238] was used to apply a gold speckle pattern to the surface of the sample. After sputtering a ~30 nm gold layer onto the surface of the sample with an Edwards S150B sputter coater, the sample was placed on a hot plate at 150 °C in a styrene-argon atmosphere. After four days of remodelling, distinct gold speckles of ~ 5-20 nm were present consistently across the sample. The sample was cooled slowly to promote the formation of delta hydrides. The images for HRDIC analysis were acquired using an FEI Magellan HRFEG-SEM, in Back-Scattered Electron (BSE) imaging mode at an accelerating voltage of 5 kV with a 2 kV stage bias, a 0.8 nA current and at a working distance of 3.6 mm. These conditions were used in immersion mode to enable individual gold speckles to be clearly defined compared to the substrate. To achieve speckles with an

average size of 3 pixels, a horizontal field width (HFW) of 10  $\mu$ m at a resolution of 2048 x 1768 pixel<sup>2</sup> was used with a dwell time of 10  $\mu$ s to minimise noise. In order to study a statistically relevant area, an array of 12 x 12 images<sup>2</sup>, which equates to a total area of 110 x 95  $\mu$ m<sup>2</sup> (after accounting for overlap), was captured using FEI MAPS with a three-point focus interpolation to ensure accurate focus across the entire region of interest. The images for each deformation step were stitched together using the 'Grid/Collection stitching' function in ImageJ [36] with a linear blend applied between images. Grain orientation maps of the HRDIC region were also obtained with the FEI Magellan HRFEG-SEM and an AZtec EBSD system and an Oxford Instruments Nordlys II detector, at an operating voltage of 20 kV and a step size of 0.1  $\mu$ m. Patterns were acquired at a resolution of 168 x 128 pixels<sup>2</sup>. Three phases were indexed, namely the HCP zirconium matrix, FCC delta hydride and HCP Zr(Fe,Cr)<sub>2</sub> SPP. Phase identification was also carried out with glancing angle (3° incident beam and ~1.6  $\mu$ m penetration depth) X-ray diffraction on a Philips X'pert diffractometer equipped with a 40 kV copper tube.

#### Deformation and image correlation

Ex-situ uniaxial tensile deformation was carried out, at room temperature, using a Kammrath-Weiss 5 kN microtester at an initial strain rate of 1.6 x 10-4 s<sup>-1</sup> to macroscopic plastic strains of ~1%, ~2% and ~3%. The images acquired at each deformation stage were shift corrected relative to the undeformed image to remove any rigid body translation or rotation. HRDIC analysis was then performed using the commercially available LaVision Davis 8.4 software, using a Fast Fourier Transform (FFT) correlation method. It was performed iteratively, starting with an initial interrogation window size of 1024 x 1024 pixel<sup>2</sup> down to a final interrogation window size of 16 x 16 pixels<sup>2</sup>, corresponding to 78 x 78 nm<sup>2</sup>. The in-plane displacement vector field (u, v) was then exported from Davis and imported into the DefDAP 0.9 Python package [263]. The strain in loading direction is given as  $\varepsilon_{xx} = \frac{du}{dx}$ , the strain in normal direction as  $\varepsilon_{yy} = \frac{dv}{dy}$  and the in-plane shear as  $\varepsilon_{xy} = \frac{du}{dy} + \frac{dv}{dx}$  in order to better visualise the data, effective shear strain is used [167,174] and is given as:

$$\gamma_{\text{eff}} = \sqrt{\left(\frac{\varepsilon_{\text{xx}} - \varepsilon_{\text{yy}}}{2}\right)^2 + \left(\frac{\varepsilon_{\text{xy}}}{2}\right)^2} \tag{1}$$

For small deformations, the amount of rigid body rotation about z is given as [186]:

$$\omega_3 = \frac{1}{2} \left( \frac{\mathrm{d}u}{\mathrm{d}y} - \frac{\mathrm{d}v}{\mathrm{d}x} \right) \tag{2}$$

An affine transform was applied to the EBSD map to transform it to the HRDIC reference frame. This transformation was calculated by defining homologous points between each dataset using the DefDAP Python package [263]. Subsequently, the angles of the active slip trace(s) were defined for each grain. The active slip system(s) in each grain was determined by comparing these angles to the theoretical slip trace angles calculated from the average grain orientation [245]. The slip planes considered were basal (1), prismatic (3) and firstorder pyramidal (6). An acceptance angle of ±5 degrees was chosen and if more than one slip system lies within this criterion this grain is disregarded from slip system activation statistics.

## Results

#### Hydride morphology

Prior to homogenisation, the hydrogen rich rim on the surface of the sample was observed with optical microscopy and a differential interference contrast prism (Figure 7.2a) to have a thickness of around 10  $\mu$ m. Glancing angle X-ray diffraction phase analysis indicated the presence of only delta hydride [264]. EBSD analysis, shown in the IPF ND map in Figure 7.2b showed the H rim to consist of columnar grains aligned approximately perpendicular to the surface. Although there are few cases where metal and hydride are indexed directly adjacent to each other, the  $\{0001\}_{M} || \{111\}_{H} \& <11-20>_{M} || <110>_{H}$  orientation relationship is observed in the majority of those cases (~60% within ±5 degrees). No other distinct relationship was observed.



**Figure 7.2.** a) Optical micrograph and b) IPF ND orientation map of zirconium matrix and delta hydride from EBSD of as-charged microstructure showing a ~10  $\mu$ m hydride rim. c) BSE micrograph and d) magnified BSE micrograph of microstructure in bulk after homogenisation heat treatment. Large transgranular hydrides are highlighted by dashed red lines. Examples of smaller intergranular hydrides are denoted by red arrows.

After homogenisation, large globular transgranular hydrides aligned approximately in TD are observed (Figure 7.2c and within dashed red lines in Figure 7.2d). These have a width of ~2-10  $\mu$ m and a length of ~10-250  $\mu$ m. Smaller intragranular hydrides up to ~1  $\mu$ m in size are observed within grains (denoted by arrows in Figure 7.2d). The large size of transgranular hydrides and presence of a large number of intergranular hydrides, which may be due to a concentration gradient still remaining from the rim, gives an opportunity to more easily investigate the strain localisation within a hydride and allows comparison between different hydride morphologies.

#### Hydride microstructure

An EBSD map of the HRDIC region after deformation is shown in Figure 7.3a, with the hydride coloured in IPF Z colouring and the zirconium matrix in white with grain boundaries highlighted in black. The region of interest contains a large transgranular hydride, around 65 x 10  $\mu$ m<sup>2</sup>, with smaller intragranular hydrides in the surrounding grains as well as a number of second phase particles. Delta hydride was indexed in 10.2% of the total area and the Zr(Fe,Cr)<sub>2</sub> SPP was indexed in 0.6% of the points. The size of the second phase particles in the material investigated reaches ~700 nm. The majority of the map consists of zirconium matrix (83.4% of the total points). Non-indexed points make up 5.8% of the total points and are concentrated in areas adjacent to hydrides, especially the large transgranular hydrides.

The  $\{0001\}_{M} || \{111\}_{H} \& <11-20>_{M} || <110>_{H}$  orientation relationship is observed between the hydrides and zirconium matrix (>80% within ±5 degrees). The angular deviation from the orientation relationship is shown in Figure 7.3b. The offset from zero and the spread in this distribution may be a result of deformation, since the EBSD map was acquired after ~2.6% strain. No other distinct orientation relationship apart from  $\{0001\}_{M} || \{111\}_{H} \& <11 20>_{M} || <110>_{H}$  was observed. The largest mean relative misorientation from the mean grain orientation (1.1°) is observed for the zirconium hydride phase. A larger degree of misorientation was generally observed for larger hydrides. The smallest mean relative misorientation from the mean grain orientation (0.4°) is observed in the second phase particles.

From the orientation relationship, the location of the prior zirconium matrix boundaries within the transgranular hydrides can be determined and are shown in white in Figure 7.3a. As a result of the orientation relationship between the alpha zirconium matrix and the delta hydride, different hydride crystallographic orientations, or "variants", can be observed for a given zirconium matrix orientation. In the transgranular hydrides, two variants are always observed for a given zirconium matrix grain. It should be noted that the two variants of hydride for a given zirconium matrix orientation are {111}<11-2> twins, which are likely caused during precipitation as a mechanism to relieve the misfit stress induced by the volume expansion from zirconium matrix to zirconium hydride. In most cases, a single

variant or one dominant variant is observed in the intergranular hydrides for a given zirconium matrix grain. However, for larger intergranular hydrides, a second variant is sometimes observed.



**Figure 7.3.** a) IPF Z map for zirconium hydride, obtained from EBSD, with zirconium grain boundaries in black. Blue arrows point to  $\{10-12\}<-1011>$  tension twins. b) angular deviation from the  $\{0001\}_{M}||\{111\}_{H} \& <11-20>_{M}||<110>_{H}$  orientation relationship. c) relative misorientation distribution for zirconium matrix, zirconium hydride and SPP.

#### **Strain localisation**

Figure 7.4a shows a phase map of the region of interest, obtained from EBSD and transformed to the HRDIC reference frame using an affine transformation. An effective shear strain map of the same region following deformation to 3% macroscopic strain is presented in Figure 7.4b. The phase boundaries are shown in black, where the adjacent non-indexed points have been assumed to be the hydride phase for clarity. The grain boundaries in the zirconium matrix are shown in white.

Fine, diffuse slip is observed in most of the matrix, with evidence of strain localisations near grain boundaries. However, effective shear strain localisations of over 10% are observed in a band at 45° to the loading direction, which is denoted by the rightmost red diagonal box

in Figure 7.4b and named 'high strain band'. Adjacent to this band is an area with comparatively little deformation with an average effective shear strain of 1.7% compared to 3.7% for the high strain band and 2.7% for the entire map. This area is denoted by the leftmost red diagonal box in Figure 7.4b named 'low strain band'. Bands of alternating lower and higher strain at 45° to the loading direction have been previously observed in non-hydrided zirconium alloys [180,185,238], suggesting they are not directly a result of hydrides. Nonetheless, the partitioning of strain will be compared between these two bands later.

The large transgranular hydride in the centre of Figure 7.4b spans both of these bands. The effective shear strain localisations of over 10% within the high strain band occur near the matrix-hydride boundaries and on a sub-grain scale in shear bands in matrix grains away from the hydride. Slip from the matrix can be seen to terminate on reaching the transgranular hydride in a number of places, two of these are highlighted by dotted white boxes and are characterised in detail later. The shear bands which appear to be within the transgranular hydride in Figure 7.4b, denoted by white arrows, mostly correspond to non-indexed points and therefore are not definitively the hydride phase. Nonetheless, a diffuse shear is still present in the lower half of the hydride. The influence of smaller intergranular hydrides is more difficult to assess due to their small size and the generally diffuse nature of slip in the matrix and the strain within these will be assessed statistically in the next section.



a) 📕 Metal 📃 Intragranular δ-ZrH 📕 Transgranular δ-ZrH 📕 SPP 🗌 Non-indexed

**Figure 7.4.** a) Phase map of the region of interest obtained from EBSD. b) Effective shear strain map for the same region obtained using HRDIC, following deformation to ~3% macroscopic strain. Red boxes and white dotted boxes illustrate regions which are discussed in detail later.

## Strain frequency distribution

The strain frequency distribution for the map shown in Figure 7.4b is shown in Figure 7.5a for the zirconium matrix, the large transgranular hydride, smaller intragranular hydrides and  $Zr(Fe,Cr)_2$  SPP. Non-indexed points from EBSD are not included in this analysis. The mean effective shear for all phases in the entire region of interest is 2.7%. Since the SPPs are small (areas of 1-35 pixels, corresponding to 0.01-0.35  $\mu$ m<sup>2</sup>) and there is some alignment error between the HRDIC and EBSD maps, single pixel SPPs are not included in the analysis. Nonetheless, the median strain within SPPs is 0.8%, compared to 1.7% in the metal.



**Figure 7.5.** Strain frequency distribution for zirconium matrix, transgranular hydride, intragranular hydrides and second phase particles for a) the entire map, b) the high strain band and c) the low strain band, all for the ~3% deformation step. Mean, 0.1<sup>st</sup> percentile and 99.9<sup>th</sup> percentile for each phase in the inset table.

To assess the impact of the alternating macroscopic bands of high and low strain (discussed earlier) on the partitioning of strain to the hydride, two regions were selected for comparison, denoted by the red boxes in Figure 7.4b. In the band on the right, the mean strain for all phases is 3.7% and the histogram for the region is shown in Figure 7.5b. The average strain in the hydride phase is 3.3% compared to 3.9% in the metal and 3.0% in the SPP. In the band on the left, the average strain in all phases is 1.7% and the histogram for the region is shown in Figure 7.5b. The average strain is shown in Figure 7.5b. The average strain in the hydride phase is 1.7% and the histogram for the region is shown in Figure 7.5b. The average strain in the hydride phase in this region is 1.5% compared to 1.8% in the metal and 1.6% in the SPP. These histograms show that the bimodal nature of strain in the hydride is likely a result of deformation banding, since the

histograms for the hydride in both bands show a unimodal distribution. However, in both the low and high strain bands less strain is observed within the hydrides and SPPs compared to the matrix. The residual bimodal distribution of strain in SPPs may be a result of the alignment error, where high strain values in the matrix adjacent to SPPs are included in the histogram.

The histograms above show only the data from the final deformation step. However, the amount of strain in the hydride, as a function of the strain in the zirconium matrix, decreases with increasing deformation, from 0.893 at ~0.8% macroscopic strain to 0.858 at ~2.6% macroscopic strain. This change is larger for the transgranular hydride, as illustrated in Figure 7.6.



*Figure 7.6. Effective shear strain in matrix, intergranular hydrides and transgranular hydrides for the three deformation steps.* 

#### Slip system activity

By comparing grain orientations from EBSD to the slip plane observed from HRDIC, the active slip systems in the material were calculated. The results are summarised in Table 7.11. In around 50% of cases, no suitable match was found, either because no slip plane was identified within ±5 degrees or more commonly because two or more unique slip planes exist within ±5 degrees due to the texture. These cases were discounted from further analysis. The primary slip system activated is prismatic slip, which indicates no change as a result of hydriding. Two instances of {10-12}<-1011> tension twins are also

observed within the HRDIC region and are highlighted with arrows in Figure 7.3. Since no grains have their c-axis within 45 degrees of the loading direction, the mechanism by which these twins formed is unclear however both twins are adjacent to hydride precipitate. Outside the HRDIC region, a further three twins are observed, two of which are adjacent to a hydride.

## Discussion

The  $\{0001\}_{M} || \{111\}_{H} \& <11-20>_{M} || <110>_{H}$  orientation relationship is observed between the hydrides and zirconium matrix in the as-charged and homogenised states. In some cases where the relationship is not obeyed, it is because an intergranular hydride has grown into a grain boundary, forming a boundary with an adjacent Zr grain. The orientation relationship observed here is consistent with previous studies for  $\delta$ -hydride in Zircaloys, precipitated under no stress [124,132,139–146]. The larger hydrides generally exhibited {111}<11-2> twinning between two hydride variants, in agreement with literature [159,265]. Both these variants obeyed the orientation relationship for the parent zirconium matrix grain. As twinning was especially prominent in the large transgranular hydride it is likely to be a mechanism to reduce stress build-up as a result of the anisotropic misfit strain accumulated during precipitation of the hydride. The smaller intergranular hydrides generally only have one variant. Prior to homogenisation, only delta hydride was observed, in agreement with a previous study by Blat et al. [154], but in contrast to a more recent study by Birch et al. [139] where only  $\varepsilon$ -hydride were observed.

From EBSD, more misorientation is observed within the hydride phase compared to the matrix, with more misorientation seen especially in the large transgranular hydride. This is consistent with previous observations from EBSD [265] and X-ray diffraction [258], which show an increased misorientation and dislocation density in hydrides upon precipitation as a result of misfit strains between the matrix and hydride. Since the map in this study was acquired post-deformation, it is unclear whether this is a result of hydride precipitation or deformation, however they are both likely to contribute. Increasing geometrically necessary dislocation density with deformation at a matrix-hydride boundary has been previously observed in in-situ using high angular resolution electron backscatter diffraction micropillar deformation [259].

The primary slip system activated in hydrided Zircaloy-4 was found to be prismatic, which is the same as observed in non-hydrided Zircaloy-4 as summarised in Table 7.1 [245,262]. However, more pyramidal slip is observed in the hydrided samples compared to the non-hydrided samples (84% compared to 94-96%, considering only slip and not twinning). Tension twinning {10-12}<-1011> was also observed however, which would not be expected given the texture of the material. No twinning is observed in non-hydrided zirconium deformed along RD, since there are few grains aligned with their c-axis along the loading direction [245]. This is also the case here, as shown in the IPF Figure 7.3c. The reason for the twinning is currently unclear.

**Table 7.1.** Slip system activation in current study compared to literature for samples deformed alongRD.

Study (strain \ temp)	Material condition	Number (percentage) of grains with activated slip/twin systems				
		Pr	Ва	Ру	Tw	
This study (3% \ 25°C)	Hydrided	27 (79%)	0	5 (15%)	2 (6%)	
Thomas et al. [262] (2.2% \ 25°C)	Non- hydrided	124 (96%)	0	5 (4%)	0	
Thomas et al. [245] (2% \ 25°C)		31 (94%)	0	2 (6%)	0	

## Zirconium-hydride boundary

To investigate in more detail the impact of hydrides on strain localisation in the studied material, two regions from dotted boxes in Figure 7.4 are shown in Figure 7.7 b and d, together with IPF Z maps from EBSD in Figure 7.7 a and c. Due to the orientation relationship between the zirconium matrix and the hydride, the location of the prior-matrix grain boundary can be approximately determined and is denoted by a red dotted line. In both cases, shear bands are seen to terminate near the matrix-hydride grain boundary
(denoted by stars in Figure 7.7). In the case of the starred region in Figure 7.7b, both hydride variants have a slip plane well aligned with the incoming slip plane from the matrix. This is also the case for one variant in the starred region in Figure 7.7c. HRDIC measurements do not capture the microscopic arrangement of hydride platelets however and this is likely to have an influence on slip transmission as noted by Weekes et al. [159]. It was noted in the aforementioned study that delta hydride was more likely to deform in the plane of the hydride platelets i.e. between the hydride platelets. However, assuming the microscopic hydride platelets are precipitated on the basal plane in this study, it is possible that only basal slip from the zirconium matrix will propagate into the macroscopic hydride. Since only prismatic and pyramidal slip are seen in Zircaloy-4 deformed along RD, slip transmission between the matrix and hydride would be more difficult. Deforming a sample along TD would therefore be beneficial to test this hypothesis.

In some cases, however, there appears to be large effective shear strains within the hydride (denoted by arrows in Figure 7.7b and d). In these areas, a large proportion of non-indexed points are present in the EBSD map (as denoted by the black pixels in Figure 7.7a and c). It is therefore not possible to definitively conclude that these large strain values correspond to the hydride phase. Nonetheless, diffuse effective shear strain is observed in regions that are conclusively hydride, as suggested by the histogram data. Some deformation may therefore be accommodated in the hydride.



**Figure 7.7.** a) and c) IPF Z orientation map for the hydride phase, with crystal orientations and slip planes for matrix and hydride and b) and d) effective shear strain map for same regions. Both regions are taken from dotted boxes in Figure 7.4. Approximate prior zirconium matrix grain boundaries are illustrated with dashed red lines.

### Second phase particles

As well as the hydride phase, and area fraction of ~0.6% of hexagonal Zr(Fe,Cr)<sub>2</sub> second phase particles were also indexed by EBSD. In the map, SPP size varies from 0.01  $\mu$ m<sup>2</sup> (limited by the EBSD step size) to 0.35  $\mu$ m<sup>2</sup>. Of all the SPPs indexed, 57% are adjacent to a hydride, which is more than would be expected considering the hydride only occupies an area fraction of ~10%. Within the large transgranular hydrides, a disproportionately high fraction of SPPs are observed (an area fraction of ~1.2%). This observation seems to agree with previous suggestion that SPPs may act as intra-granular nucleation sites for hydrides [266]. These SPPs can be also observed in the strain map as having very little strain within them, as suggested by the lower average strain in the SPPs. Figure 7.8 shows a small subset of the region of interest, which contains three large (700-1000 nm diameter) SPPs, two conjoined at the zirconium matrix grain boundary and another  $\sim 1 \ \mu m$  away. Within each particle, almost no effective shear strain is observed compared to the surrounding matrix, where strains of up to 8% are measured. In the SPP away from the grain boundary, undeformable particle behaviour is observed, with lobes of positive rotation on two sides of the precipitate and two alternate lobes of negative rotation. An increased amount of shear is also observed in the adjacent slip bands. The two conjoined SPPs closer to the grain boundary each have a different crystallographic orientation, the boundary is denoted by a white line within. In all second phase particles, almost no effective shear strain is observed within, compared to ~3% in the surrounding matrix.



**Figure 7.8.** a) Phase map from EBSD, b) effective shear strain map from HRDIC and c) rotation map from HRDIC for a region containing two Zr(Fe,Cr)2 SPPs from dotted box in Figure 7.4. Black lines illustrate phase boundaries and white lines illustrate the approximate zirconium matrix grain boundary position.

Since the hexagonal Zr(Fe,Cr)<sub>2</sub> SPP are present at a low volume fraction and the localisations seen are no more severe than generally observed in the matrix, it is unlikely to affect deformation behaviour. However, the lobes of positive rotation on two sides of the precipitate and two alternate lobes of negative rotation has been predicted using CPFEM, albeit in an Al-Si alloy SPPs, suggesting their effect in zirconium alloys could be modelled to be further studied [188].

### Conclusions

Strain localisation in a hydrided Zircaloy-4 sample, deformed to 3% strain in uniaxial tension along RD was measured using HRDIC, in a region containing a large transgranular hydride and smaller intragranular hydrides. The strain data was related to phase and grain orientation information, determined from EBSD. The key findings are as follows:

- The  $\{0001\}_{M} | | \{111\}_{H} \& <11-20>_{M} | | <110>_{H}$  orientation relationship is observed between  $\delta$ -ZrH<sub>1.66</sub> and  $\alpha$ -Zr for the homogenised microstructure. The exceptions to this orientation relationship normally occur when hydride growth reaches a zirconium matrix grain boundary. Smaller intergranular hydrides usually only contain one variant whereas larger hydrides generally contained two twinned variants, which is likely to alleviate stresses generated during precipitation as a result of anisotropic misfit strains.
- The mean effective shear strain in the  $\delta$  hydride phase is 13% lower than that in the metal. In the large, transgranular hydride, the mean strain is 19% lower than that in metal, whereas the mean strain is 9% lower than that in the metal for the smaller, intragranular hydrides. The misorientation observed in the hydride was larger than in the matrix however, although it is likely this (at least in part) predicated the loading.
- The primary slip system observed in the zirconium matrix was prismatic <a>, suggesting no change to primary slip system as a result of hydrides, although more pyramidal slip was observed compared to non-hydrided material. Tension twinning {10-12}<-1011> was adjacent to hydrides however, the reason for which is unclear.
- Of all the Zr(Fe,Cr)<sub>2</sub> SPPs indexed by EBSD, 57% are adjacent to a hydride, with a higher density within the transgranular hydride. This suggests SPPs may act as nucleation sites for hydrides. The Zr(Fe,Cr)<sub>2</sub> SPPs also exhibit a mean strain 16% lower

than matrix, with a narrower strain distribution. Spatially, undeformable particle behaviour is observed, with lobes of positive rotation on two sides of the precipitate and two alternate lobes of negative rotation.

 Shear bands from the zirconium matrix were observed to stop at the hydride-matrix boundary, with only limited evidence of shear bands in a hydride due to non-indexed points in EBSD. However, diffuse shear was observed within the hydride, primarily near strain localisations in the zirconium matrix, suggesting the hydride can accommodate some deformation.

### 8. Conclusions

The aim of this project was to further the understanding of the deformation behaviour in zirconium alloys and assess the impact of irradiation and hydrides, which cladding is subjected to in service. An SEM-based strain mapping technique known as HRDIC was used in conjunction with EBSD to relate underlying microstructure to shear localisation with a resolution of <0.1  $\mu$ m in areas of >10,000  $\mu$ m<sup>2</sup>, corresponding to >100 grains. This thesis consists of four manuscripts in which a patterning technique was optimised and the first high resolution strain maps of a zirconium alloy were presented (manuscript 1), the initial assessment effect of proton irradiation on strain localisation is reported (manuscript 2), the influence of loading direction on irradiation-enhanced strain localisation investigated in more depth (manuscript 3) and finally the impact of hydrides and SPPs on deformation behaviour was quantified (manuscript 4).

# Manuscript 1

Reliable strain measurements using HRDIC require a pattern on the surface of the sample with suitable scale for the spatial resolution targeted. Ideally, the pattern should be random, dense and be consistent across the sample. The vapour-assisted gold remodelling technique provides such a pattern, but the quality depends on parameters such as vapour composition, temperature and time. For example, zirconium alloys remodelling with a water vapour produces an oxide which obscures the deformation of the zirconium matrix. This manuscript provided details on the remodelling of samples in styrene-vapour at a temperature of 200°C.

- After four days, a uniform pattern with high contrast suitable for HRDIC was achieved across the sample. The pattern generated was smaller than patterns produced with water vapour remodelling, allowing for a higher resolution to be achieved but necessitating the use of a high-resolution FEG-SEM.
- The first high resolution strain maps of ZIRLO were also presented where shear bands on the sub-grain scale as well as transgranular deformation bands across the region

were observed. Within shear bands, effective shear strain values of 6 times the applied strain was measured.

#### Manuscript 2

After further optimisation of the patterning technique to lower the remodelling temperature to 150°C, a strain localisation study was conducted on a Zircaloy-4 sample irradiated with protons to ~0.1 dpa and deformed along RD in the second manuscript. Each region contained at least 100 grains allowing for a statistical comparison of slip system activity. To allow for accurate comparison, a non-irradiated region of the sample was also studied under the same conditions.

- Fine, diffuse slip with localisations at grain boundaries was observed in the nonirradiated region. Due to irradiation hardening, the average strain in the irradiated region was lower than that in the non-irradiated region. Nonetheless, the strain was highly localised on the sub-grain scale in the irradiated region.
- The effective shear strain frequency distribution was wider for the irradiated region. This was attributed to deformation only occurring within dislocation channels, increasing the maximum strain observed compared to the non-irradiated region. The lack of deformation outside shear bands lead to an increased frequency of points exhibiting very little strain, compared to the non-irradiated region.
- Due to the alignment of grains approximately normal to the loading direction and the low CRSS for prismatic slip, non-irradiated and irradiated regions exhibited primarily prismatic slip, with some pyramidal activation.

#### Manuscript 3

Due to the 'split-basal' crystallographic texture observed in zirconium alloys, deformation along TD means some grains are better aligned for basal slip and twinning compared to deformation along RD. The third manuscript presented a study into the effect of loading direction on irradiation-enhanced strain localisation and slip system activation in Zircaloy-4 irradiated to ~0.1 dpa. Further optimisation of imaging conditions enabled the investigation of ~200 x 170  $\mu$ m<sup>2</sup> regions at 80 nm resolution, for two deformation steps. This meant that ~300-400 grains were contained in each region.

- Similar effective shear strain distributions were observed for deformation along TD compared to deformation along RD. Significantly increase strain heterogeneity was observed in both regions due to irradiation. Localised lattice rotations were observed where channels impinge on grain boundaries as a result of strain incompatibility.
- For deformation along RD, prismatic slip was primarily observed, however the improved statistics due to the larger number of grains studied suggest a small increase of pyramidal slip prevalence after irradiation.
- For deformation along TD, prismatic slip was the primary slip system (~50%), however pyramidal slip (~30%), basal slip (~5%) and twinning (10%) were also observed. Basal slip was generally wavy (possibly due to cross-slip) compared to prismatic and pyramidal which were planar. No significant change in slip system activation due to irradiation was observed.

# Manuscript 4

The aim of the fourth manuscript was to investigate the effect of zirconium hydride and Zr(Fe,Cr)<sub>2</sub> second phase particles on strain localisation in Zircaloy-4. By indexing the matrix, hydride and SPP using EBSD, the HRDIC data was segmented accordingly.

- The {0001}<sub>M</sub>||{111}<sub>H</sub> & <11-20><sub>M</sub>||<110><sub>H</sub> orientation relationship was observed between the matrix and hydride. In the larger hydrides, a twinned structure formed which is thought to be a way to alleviate the strain built up during growth, due to the anisotropic misfit strain between the matrix and hydride.
- The primary slip system activated was the same as for the non-hydrided sample i.e. prismatic <a>, however two instances of small {10-12}<-1011> twins adjacent to hydrides were also observed, the reason for which is not clear.
- On average, the strain in the matrix was highest, followed by the smaller intergranular hydrides, then the transgranular hydrides and second phase particles. Shear bands from the matrix were observed to terminate in the transgranular hydride.

### Impact

The methods described in the thesis and first manuscript give a basis for further digital image correlation studies to be performed on zirconium alloys and other corrosion-

susceptible materials. The software developed by the Mechanics of Microstructures group and The University of Manchester during the course of the PhD has also been released to the public (available at https://github.com/MechMicroMan/DefDAP). This software can be used to load a HRDIC strain map and link it to an EBSD map. All the data generated for this thesis was analysed using this software. This includes determining the active slip systems and performing RDR analysis in each grain.

The sub-grain scale strain measurements confirm that slip in irradiated zirconium alloys is highly localised within channels inside grains. This is consistent with previous studies which hypothesise such localisations from TEM observations. The data provided by HRDIC gives high resolution in-plane strain for many hundreds of grains however and this raw, quantitative data is published (http://dx.doi.org/10.17632/n4cdwp6pwc.1), which will allow for the further refinement of deformation models which aim to include irradiation effects. Such models may also require information on slip system activation, which has been experimentally determined and expressed statistically as well as spatially. Additionally, non-irradiated material has also been well quantified, both in terms of strain localisation and slip system activation, which is useful for accurately determining the change due to irradiation.

The effect of hydrides on strain localisation was also measured. Although the strain heterogeneity was not significantly different to non-hydrided material, a lower strain was measured in the hydride compared to the matrix. This provides quantitative insight into the extent to which hydrides are able to carry a load when they are embedded within a zirconium matrix. The magnitude of the change could be compared spatially to models attempting to assess the impact of hydrides on early deformation behaviour. Suggestions for future work which would complement and are given in the next section.

### 9. Future Work

Firstly, investigating the HRDIC region using TEM would allow comparison of the observed dislocation channel widths between the two techniques. Currently, a wider than expected dislocation channel is observed with HRDIC, compared to previous TEM studies. Focused ion beam milling could be used to extract lamellae perpendicular to the slip plane [256]. Additionally, the effect of different slip planes (i.e. basal, prismatic or pyramidal) on the clearing of loops could be further investigated. The possible observation of pyramidal <a> slip from the RDR analysis could also be confirmed using TEM.

Assessing the effect of both proton irradiation and hydrides on deformation behaviour is important, since both irradiation damage and hydrides will be present in cladding at endof-life. The sub-grain strain heterogeneity due to irradiation should make it easier to quantify the precise effect of hydride on strain localisation. This data has already been collected and will be analysed and presented in a manuscript in the future. Additionally, improving the indexing of hydrides in EBSD would also be beneficial to reduce the uncertainty with regards to the possibility of hydride shearing. Ion polishing or electropolishing might be useful in this regard.

All the work carried out here has been samples irradiated with protons to ~0.1 dpa, which is a small fraction (~2%) of the damage encountered in a component by the end of its life in-reactor [267]. The primary reason for this was to investigate the stage of irradiation where the most significant ductility decrease was observed. However, it is also possible that for higher irradiation damage levels, the amount of strain localisation in the irradiated region will increase to a point where correlation with the DIC technique may become difficult. Nonetheless, taking the sample to higher damages and macroscopic strains would be useful to investigate the link between fracture and strain heterogeneity. No significant change in slip system was observed for room temperature deformation at 0.1 dpa in contrast to a complete transition to basal channelling observed in literature for deformation at reactor operating temperature along TD after irradiation to 1 dpa. The same transition was seen following proton irradiation to 2 dpa and deformation at room

temperature. Further studies would be beneficial to ascertain the damage level at which the transition occurs. Assessing the amount of strain heterogeneity as a function of damage would also be useful. To this end, performing low resolution measurements may be beneficial to allow for the entire gauge length to be mapped. Ideally, generating a pattern suitable for low resolution DIC and high resolution DIC would give the greatest amount of information and allow for high resolution measurements to be focussed on interesting areas. Recently, crystal plasticity models have been developed to take into account irradiation damage [244,268]. In particular, a FFT modelling framework used by Marano et al. [269] show features such as kink bands which are similar to those observed experimentally in this thesis. Using the results from HRDIC, specifically the change in slip system activity due to irradiation, these models could be further refined and validated.

Due to the high magnification required as a result of the small speckles generated using the styrene-assisted vapour remodelling technique, a high-end SEM with a piezoelectric stage, immersion lens and small working distance was used for this work. As a result, an in-situ stage was not fitted which means elastic strains could not be measured. If the speckles could be made larger, or an alternative technique used, performing in-situ experiments would allow more frequent strain measurements, compared to an ex-situ experiment where the sample needs to be taken out of the SEM to be strained. The evolution of dislocation channel width with strain could then be studied.

Although Zircaloy-4 is commonly used in nuclear reactors, other zirconium alloy samples such as Zr-2.5Nb are also commonly used in different reactor types (such as the CANDU reactor). The addition of alloying elements such as Sn is known to increase the yield stress, decrease the SFE and enhance the amount of twinning in zirconium alloys [73]. It was also suggested by Krishna et al. [73] that decreasing would enhance prismatic slip planarity. The effect of alloying elements, specifically slip planarity and heterogeneity, could be investigated using HRDIC.

Validation of the strain heterogeneity behaviour with neutron irradiated material should also be carried out to ensure the results are comparable. Although it has been shown that defect structures between proton and irradiated materials are similar, subtle differences may not be clear in TEM-based studies on limited areas and these could influence deformation behaviour.

All the deformation in this thesis has been carried out at room temperature. In order to replicate in-reactor conditions, elevated temperature deformation could be performed. Edwards et al. [171] have demonstrated a method to allow speckles generated using the vapour-assisted remodelling technique to be used on deformation at up to 700°C. At higher temperatures, the CRSS of basal slip becomes more similar to that of prismatic slip [50]. Investigating deformation at higher temperatures would be especially interesting for hydrogen charged samples, where the hydrogen could be dissolved into solid solution. Investigating the mechanism behind the significant increase in the ductile to brittle transition temperature of cladding with a small amount of hydrogen would also be possible if high temperature deformation was carried out.

Although the focus of the work here is the use of digital image correlation and electron backscatter diffraction techniques, other techniques could provide complimentary information. Using a synchrotron, load partitioning between  $\alpha$ -Zr and  $\delta$ -hydride phases has been investigated by measuring the lattice strain evolution [270,271]. Dislocation densities inside hydride blisters have also been measured using line profile analysis, where it was found that  $\delta$ -hydride have a large dislocation density [258]. This could be investigated further to measure dislocation density evolution as a function of deformation, for both the  $\alpha$ -Zr and  $\delta$ -hydride phases. Measuring dislocation density in individual grains in a polycrystalline material can also be investigated in a synchrotron. Performing such measurement during deformation of irradiated materials would yield information about the clearing of channels during the early stages of plastic deformation.

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